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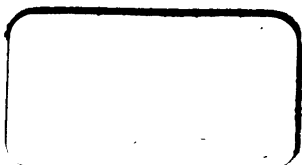


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THE ATOMIC MASS AND DERIVATIVES OF SELENIUM.<sup>1</sup>

By VICTOR LENHER.

Received June 6, 1898.

INTRODUCTION.

THE following contribution to our knowledge of selenium was undertaken with the view of studying the various derivatives and reactions of the element, and using such methods or compounds as would prove available in the determination of its atomic mass.

In the series presented, ratios have been determined in compounds differing widely in character and composition, and by methods entirely unlike in nature.

The action of hydrochloric acid gas upon the salts of acid oxides which possess the power of forming volatile compounds with it, affords a clean and accurate method, which can be used in establishing the atomic ratio.

A salt of such a character, when subjected to the action of the gas, yields a substance removed at once from the field of action, while in the vessel which contained the original salt there remains a chloride which can be directly weighed.

Such a method almost completely eliminates the factor of personal error, in that the operator needs but weigh the original

<sup>1</sup> Author's thesis for the Degree of Doctor of Philosophy.

salt and the resulting chloride, no manipulation intervening in which he is directly concerned.

If it be possible to use a salt whose resulting chloride can be directly reduced to metal, we have a means of establishing from one salt two series of ratios, which if agreeing, both as individuals and series, means that a ratio has been established comparable to that existing between the metal and its chloride. If two such series agree, a direct proof is established of the purity of material and accuracy of the method.

An ideal salt for such treatment is a salt of silver; first, since its chloride can be directly reduced to metal by heating in a current of hydrogen gas; second, the ratio between silver and chlorine is one of the most firmly established ratios. Silver selenite is an anhydrous salt, which crystallizes well, is unaffected by light, and is perfectly stable. This substance, when treated with gaseous hydrochloric acid, yields silver chloride and a hydroxychloride of selenium, corresponding in composition and properties to that obtained by A. Ditte,<sup>1</sup> when acting on selenium dioxide with hydrochloric acid gas.

In the first series of experiments, silver selenite was weighed, treated with hydrochloric acid gas, and silver chloride formed, which was weighed. In the second series, silver selenite was weighed, converted into silver chloride, which was weighed, the chloride was reduced in hydrogen to metal, and this again weighed; two ratios were thus established from one sample of selenite by comparison with silver and chlorine, and with metallic silver.

A study of all the known double bromides has been made, and new bromides of rubidium and cesium prepared. Of all the salts examined, the one which seems best adapted for the purpose of an atomic mass series is the ammonium salt. This substance is easily obtained pure and crystallizes well. When treated with hydroxylamine, selenium is set free, and the element itself can be brought on an asbestos filter, washed, dried at 100°, and weighed.

The use of hydroxylamine, according to the method of Dr. Harry F. Keller,<sup>2</sup> for the precipitation of selenium, affords the

<sup>1</sup> *Ann. chim. phys.*, (5), 10, 82.

<sup>2</sup> Private communication from the author.

clean and accurate determination that has long been desired by those who have used the tedious and uncertain precipitation by sulphurous acid or sodium sulphite in hydrochloric acid solution.

In many of the double halides which contain the ammonium group it has been possible to replace the ammonia by organic bases. This is especially the case in many of the salts of the metals of the platinum group. A series of salts has been prepared and studied in which the ammonia in ammonium bromoselenide has been substituted by fatty amines or aromatic bases. It was hoped that it would be possible to find a compound which would be of such character that it could be subjected to careful analysis. Such was not the case; none seemed to meet the demands imposed on them.

Finally a study was made of the monoxide of selenium, the existence of which has been repeatedly questioned.

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## FIRST SECTION.

### HISTORICAL.

The atomic mass of selenium has been determined by a number of workers and by various methods. Figures have been obtained which range between 78.52 and 79.35 ( $O = 16$ ).

The first to determine the atomic mass of this element was Berzelius.<sup>1</sup> He found that 100 parts of selenium, when treated with chlorine, gave 179 parts of the tetrachloride. If chlorine be 35.45, the atomic mass of selenium would be 79.22, from the single determination mentioned.

The next work was by Sacc,<sup>2</sup> who presents two series. The first includes three reductions of selenium dioxide with ammonium bisulphite and hydrochloric acid. This series gives selenium the atomic mass 78.68 ( $O = 16$ ). The second series was obtained by treatment of barium selenite with sulphuric acid, and the subsequent weighing of barium sulphate. The mean of the four determinations gave 78.52 ( $O = 16$ ,  $S = 32.07$ ,  $Ba = 137.43$ ).

<sup>1</sup> *Pogg. Ann.*, 8, 1.

<sup>2</sup> *Ann. chim. phys.* (3), 21, 119.

In 1852, Erdmann and Marchand<sup>1</sup> analyzed repeatedly sublimed and well-crystallized selenide of mercury, and obtained the figure 78.83 ( $\text{Hg} = 200$ ) ; a value between that of Berzelius and Sacc.

Eight years later, Dumas<sup>2</sup> repeated the work of Berzelius, passing chlorine over selenium. He obtained the value 79.35 ( $\text{Cl} = 35.45$ ).

In 1876, Ekman and Pettersson ignited silver selenite, metallic silver was obtained, which retained traces of selenium. Their result is 79.00 ( $\text{Ag} = 107.92$ ). They also present a second series in which selenious acid was reduced by sulphur dioxide in the presence of hydrochloric acid. The selenium was brought on a glass filter and weighed. The second series gave a mean of 79.04 ( $\text{O} = 16$ ).

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#### DETERMINATION OF THE ATOMIC MASS OF SELENIUM BY THE HYDROCHLORIC ACID METHOD.

##### PREPARATION OF PURE SILVER BY THE METHOD OF STAS.

About 100 grams of ordinary pure silver were dissolved in hot dilute nitric acid. The solution was evaporated to dryness, the mass heated to the point of fusion, and held at that temperature until the oxides of nitrogen ceased to evolve. The cold residue was dissolved in water and this solution allowed to stand forty-eight hours, when it was run through a double filter to remove any suspended matter. After diluting the filtrate with thirty times its volume of distilled water, an excess of pure hydrochloric acid was added. The silver chloride was allowed to settle, after which it was washed by decantation with water containing a little hydrochloric acid, and finally with pure water. The silver chloride was collected on a cheese-cloth filter, pressed well and allowed to dry. When perfectly dry it was digested with aqua regia for several days, after which it was again washed by decantation with water. The pure silver chloride, thus prepared, was ready for reduction with milk-sugar and caustic potash. It was then necessary to purify the milk-sugar

<sup>1</sup> *J. prakt. Chem.*, 55, 202.

<sup>2</sup> *Ann. Chem. Pharm.*, 113, 32.

and potassium hydroxide, which were to be used in reducing the chloride to metal. The potassium hydroxide was heated to boiling and treated with a strong solution of potassium sulphide to precipitate any heavy metals which might be present. After filtration, the solution was treated with freshly precipitated silver oxide, and again filtered to remove the excess of potassium sulphide. The milk-sugar which was used was purified in a similar manner. The silver chloride was placed in a large porcelain casserole and covered with a solution of caustic potash and milk-sugar. The dish was exposed to a heat of  $70^{\circ}$ – $80^{\circ}$  until complete reduction had taken place. The silver appeared as a gray-white mass. It was washed with distilled water until the washings no longer gave an alkaline reaction, after which it was digested with dilute sulphuric acid, and finally washed with dilute ammonia. The silver thus obtained was mixed with five per cent. of its weight of fused borax and ten per cent. of sodium nitrate. This mixture was fused in a clay crucible. The metal obtained was snow-white in appearance. It was dissolved in nitric acid to a clear solution. This solution was evaporated to dryness and the resulting nitrate was obtained as a pure white mass.

#### PREPARATION OF PURE SELENIUM DIOXIDE.

Several hundred grams of quite pure selenium were treated with nitric acid. The resulting selenious acid was evaporated to hard dryness, when the dioxide was formed. This was dissolved in water, filtered through a double filter, hydrochloric acid was added and sulphur dioxide conducted into the warm solution. The selenium thus produced was washed with water, until the washings no longer gave an acid reaction, finally dried and fused. Broken lumps of this material were placed in a crystallizing dish on a water-bath heated to  $70^{\circ}$ . Pure nitric acid was added to cover the mass, a brisk evolution of nitrous fumes took place, and the selenium was oxidized to selenious acid. When all action appeared to be over, the solution was evaporated to dryness to remove the excess of nitric acid. The residue was dissolved in distilled water, and the solution transferred to a porcelain dish. The solution was then carefully evaporated on an iron plate, and the heat gradually increased

until the sublimation point of selenium dioxide (about the boiling-point of sulphuric acid) had been reached. When selenium dioxide began to sublime, a glass funnel, the neck of which had been closed with cotton, was placed over the dish, the base of the funnel resting on the inside of the dish and fitting closely. Selenium dioxide is thus sublimed and collects on the inside of the funnel as white needle-like crystals, often several inches long. The dioxide was resublimed three times. When an attempt is made to sublime selenium dioxide which is slightly impure, red selenium contaminates the otherwise white deposit. Traces of organic matter or other impurities, in slight amount, cause a red coloration, but when pure no reduction takes place during the sublimation. The long white needles were carefully removed from the funnel by means of a platinum spatula, and dissolved in distilled water. To this solution pure barium hydroxide was added until further addition failed to produce a permanent precipitate. Any sulphuric acid that might be present was thus removed along with any selenic acid. The solution containing the barium precipitate was allowed to stand over night, after which it was filtered. The clear solution was evaporated to dryness in a porcelain dish, the residue heated on an iron plate, and finally sublimed into a dry glass funnel as before. The clear needle-like crystals were picked out and resublimed three times. Selenium dioxide thus formed is perfectly stable in dry air, but in the ordinary atmosphere absorbs moisture rather rapidly.

#### PREPARATION OF SILVER SELENITE.

Selenium dioxide was dissolved in water, forming selenious acid. To this a solution of pure silver nitrate was added, slightly in excess. A few drops of selenious acid were added, when a complete precipitation of both silver and selenium takes place. The resulting white selenite of silver was thoroughly washed with water by decantation. The water was drained off as completely as possible, and the white mass dried by gentle heat. The powder was treated with pure nitric acid, one part to three parts of water, and heated. On cooling, silver selenite crystallizes from such an acid solution as an anhydrous salt, consisting of flat plates. These plates were broken up, washed



well with water, and again treated with dilute nitric acid. The salt was recrystallized three times. Finally the selenite was thoroughly washed with water and dried by heating to 70°–80° in an air-bath for twelve hours. The salt was carefully tested for nitrate and nitric acid, but none were found to be present.

A bottle of the material prepared was allowed to remain in direct light for a period of twelve months, and at the end of that time showed no discoloration.

By comparison of a known weight of the salt with pure benzene, the specific gravity of selenite of silver was found to be 5.9297.

#### DESCRIPTION OF APPARATUS.

Hydrochloric acid was prepared by the method which has been found very satisfactory in this laboratory, and consists in evolving the gas by adding concentrated sulphuric acid to concentrated aqueous hydrochloric acid. The hydrochloric acid was contained in a three-liter flask, and sulphuric acid was dropped on it from a separatory funnel. By regulating the current of sulphuric acid with a stop-cock, a constant evolution of gas is obtained at the ordinary temperature. Only pure acids were used, and such being the case, it was sufficient to dry the gas by passing it through two wash-bottles containing concentrated sulphuric acid, and a tower containing broken pieces of anhydrous calcium chloride. The dry gas was conducted through a combustion tube of hard glass, in which was placed a weighed quantity of silver selenite. The posterior portion of the tube was bent and directly connected by means of a stop-cock with a glass bulb containing water.

#### CORRECTIONS.

The weights used were carefully calibrated, first by comparison against each other, then against a normal weight. The larger weights were of brass, gold plated, the smaller ones being of platinum. All weights given have been reduced to vacuum. The following formula was used :

$$W = P + P_{\sigma} \left( \frac{1}{A} - \frac{1}{B} \right)$$

Where  $P$  = weight of substance,  
 $\sigma$  = density of the air,  
 $\Delta$  = specific gravity of the substance,  
 $B$  = specific gravity of the weights.

The balance used was a short-arm Becker, the sensibility of which was determined to be one-twenty-fifth of a milligram.

#### METHOD OF PROCEDURE.

By allowing gaseous hydrochloric acid to come in contact with selenium dioxide, A. Ditte<sup>1</sup> formed  $\text{SeO}_2 \cdot 2\text{HCl}$ . He states that the compound consists of brilliant scales, which at  $26^\circ$  decompose into an amber-colored liquid of the composition  $\text{SeO}_2 \cdot \text{HCl}$ .

In performing the following experiments, the method of procedure was to weigh a definite amount of silver selenite into a previously weighed porcelain boat, introduce the boat into the combustion tube, and start the current of gas. After allowing the gas to pass over the salt for at least half an hour in the cold, a small flame was brought under the tube, and the boat gently heated. When the gas comes in contact with the selenite, rapid absorption takes place, the salt assuming a yellow color, due to the formation of the hydrochloride. In order to avoid any loss by spattering, as the salt becomes slightly moist, the boat was covered with a piece of platinum foil, and the heat increased very gradually. When it was thought that the selenium dioxide had been completely expelled, the tube was allowed to cool, and the boat removed to a desiccator containing soda-lime. After standing several hours, the silver chloride was weighed, replaced in the combustion tube and the gas conducted over it for one-half hour longer. The tube was again heated, and the chloride brought just to the point of fusion. It was again replaced in the desiccator, allowed to stand several hours, and reweighed. In all cases the weights of the boat before and after this second treatment were the same, a point which seems to indicate that silver chloride sustains no perceptible loss when brought to the point of fusion. The silver chloride was tested for selenium, but none was found.

<sup>1</sup> *Ann. chim. phys.*, (5), 10, 82.

Ag <sub>2</sub> SeO <sub>3</sub> . Grams.	AgCl. Grams.	Se. Atomic mass.
0.98992	0.82715	79.326
1.59912	1.33600	79.373
2.70573	2.26087	79.320

Mean = 79.339

Probable error =  $\pm 0.011$

Having thus demonstrated that hydrochloric acid gas will completely drive out selenium dioxide from silver selenite, leaving behind pure chloride, according to the equation,



the next step was to reduce the chloride formed by this reaction to metal.

#### SECOND SERIES.

Hydrogen gas was generated by the action of dilute sulphuric acid on mossy zinc. The gas was purified by conducting it through a series of wash-bottles; the first containing silver sulphate; the second, potassium permanganate; the third, lead nitrate; and the fourth, caustic potash. It was then dried by passing through sulphuric acid. The pure gas was conducted through a tube of porcelain in which the reduction took place. The excess of hydrogen and the hydrochloric acid formed were passed through a wash-bottle containing sulphuric acid, following which was a wash-bottle containing water to absorb the hydrochloric acid. The unused hydrogen was allowed to escape into the room.

The boat containing the silver chloride, after being weighed for comparison with silver and oxygen, was introduced into the porcelain tube, all connections were closed and a brisk current of hydrogen conducted through the apparatus. When the hydrogen was free from air, the combustion furnace, containing the porcelain tube, was started and the heat gradually increased until the outside of the tube attained bright redness. This temperature was maintained for a period of three hours, when the tube was allowed to partially cool, the boat and its contents were removed to a desiccator. After standing several hours, it was weighed, replaced in the combustion tube, and hydrogen again conducted over it at a red heat for an hour. The boat was again removed to a desiccator, cooled as before, and reweighed.

The weights before and after reignition in hydrogen were in all cases the same. After the last weighing, the boat and contents were treated with pure dilute nitric acid and warmed. Complete solution ensued, showing the reduction of silver chloride to metallic silver had been complete. Tests were made for selenium in the resulting solution, but none was found.

Ag <sub>2</sub> SeO <sub>3</sub> . Grams.	AgCl. Grams.	Se. Atomic mass.	Ag. Grams.	Se. Atomic mass.
0.26204	0.21897	79.299	0.16480	79.356
0.58078	0.48522	79.371	0.36534	79.280
0.70614	0.58999	79.350	0.44417	79.301
0.80811	0.67532	79.282	0.50821	79.369
0.98396	0.82232	79.263	0.61882	79.358
1.29685	1.08350	79.361	0.81562	79.277
1.63103	1.36288	79.316	1.02588	79.320
2.00162	1.67234	79.358	1.25884	79.357
		Mean 79.325		
		Probable error $\pm 0.009$		
			Mean 79.329	
			Probable error $\pm 0.009$	

#### EXPERIMENTS WITH SODIUM SELENITE.

In order to ascertain if the alkaline selenites would prove as well adapted for treatment with hydrochloric acid gas as the silver salt, a study was made of sodium selenite.

Sodium carbonate was purified by recrystallization several times. It was found, when tested, to be free from sulphate, chloride, and silicate. The salt was fused in a platinum crucible under a blast-lamp. Equivalent weights of the carbonate and selenium dioxide were dissolved in water, the solutions combined and evaporated to dryness. The salt obtained was recrystallized seven times from water. Crystallization takes place only when the liquid has attained the consistency of a thick sirup. The salt obtained in this manner, when treated with dilute hydrochloric acid, showed the presence of a slight amount of carbonate, hence was rejected.

An attempt was made to prepare the sodium salt by ignition of the acid selenite. In this case, a salt of constant composition could not be obtained. At a temperature slightly above that of complete conversion into neutral selenite, the salt appears to lose slight amounts of selenium dioxide, varying with the temperature.

DETERMINATION OF THE ATOMIC MASS OF  
SELENIUM BY ANALYSIS OF AMMONIUM  
BROMOSELENATE.

In the following part, devoted to the double bromides, a study has been made of a large number of derivatives. It is sufficient to state here that the salt found most suitable for careful analysis is the double bromide of ammonium and selenium. A description of the properties of the salt is entered into more fully in Section II.

## PREPARATION OF PURE BROMINE.

Bromine was purified by distillation over manganese dioxide and concentrated sulphuric acid. A retort containing this mixture was heated on a water-bath and the distillate collected in a chilled receiver. This product was brought in contact with manganese dioxide and again distilled. Having started with pure bromine of commerce, chlorine and organic matter would, if present, be eliminated by this procedure.

## AMMONIUM BROMIDE.

So-called "pure" ammonium bromide was twice recrystallized, the crystals dried each time by pressing between pieces of filter-paper. It was then twice sublimed and again crystallized. The salt was allowed to remain for several days in a desiccator to become thoroughly dry. Thus obtained, ammonium bromide is pure white, dissolves in water to a clear colorless solution, and on ignition leaves no residue.

## SELENIUM.

Selenium dioxide, purified in the manner previously described, was dissolved in water containing hydrochloric acid. Sulphur dioxide, generated by the action of sulphuric acid on copper turnings, was washed by sulphuric acid and conducted into the warm solution. Selenium was precipitated. It was washed with hot water until the washings no longer gave an acid reaction. After drying it was fused to the black glassy modification. While yet liquid, the mass was poured from the crucible in which it had been fused, on a porcelain plate, allowed to cool, and finally broken into small fragments.

## AMMONIUM BROMOSELENATE.

Nine and eight-tenths parts of ammonium bromide were dissolved in water; to this solution four parts of selenium were added, bromine was introduced till in slight excess, and perfect solution had ensued. The solution of ammonium salt was brought on a water-bath, the excess of bromine expelled and allowed to slowly evaporate, when ammonium bromoselenate separated. The crystals were removed from the mother-liquor, dried by pressing between filter-paper, dissolved in water containing hydrobromic acid, which had been repeatedly distilled, and allowed to crystallize at the temperature of a water-bath. The crystallization was repeated several times. Finally, the salt was placed in a desiccator containing soda-lime where it remained several days. Examined under the microscope, the red crystals showed no admixture of ammonium bromide. The specific gravity of the salt was determined in benzene and found to be 3.3266.

## METHOD OF PROCEDURE.

A weighed quantity of the salt is dissolved in water, and to this is added a few cc. of ammonia. Pure hydroxylamine hydrochloride is introduced in slight excess, when a reaction takes place, probably as expressed in the following equation:



Selenium appears in the cold as a flocculent red precipitate. The solution is gradually warmed to expel free ammonia, and render the solution neutral. Under the influence of heat the precipitated selenium changes to the gray variety. The precipitate is brought upon asbestos felt, prepared by pouring asbestos suspended in water into a Gooch crucible, and sucking hard and dry by means of a good filter-pump. This filter, having been ignited and weighed, the solution containing the selenium is poured upon it, the selenium washed thoroughly with hot water, dried for two hours in an air-bath heated to 100°, and allowed to cool in a desiccator. The increase in weight of the crucible represents the selenium in the original salt. All of the filtrates were preserved, evaporated together, and tested for selenium, but none could be detected, showing the precipitation was complete.

(NH <sub>4</sub> ) <sub>2</sub> SeBr <sub>6</sub> . Grams.	Se. Gram.	Se. Atomic mass.
1.00059	0.13324	79.243
1.50153	0.20022	79.367
2.00059	0.26649	79.273
2.00126	0.26657	79.269
3.00125	0.39958	70.226
4.00216	0.53346	79.333
5.00218	0.66656	79.306
5.03001	0.66998	79.267

Mean 79.285

Probable error =  $\pm 0.011$

Mean from silver chloride, 79.329 (11 determinations).

Mean from metallic silver, 79.329 ( 8 " ).

Mean from analysis of ammonium bromoselenate, 79.285 ( 8 " ).

Giving a general mean, 79.314

The values used in calculation are those given by Clarke (Atomic Weights, 1897), and are as follows :

Ag .....	107.92
Br .....	79.95
Cl .....	35.45
O .....	16.00
N .....	14.04
H .....	1.008

The mean of all determinations is close to the values obtained in the synthesis of selenium chloride being slightly higher than the determination by Berzelius and a trifle lower than the series of Dumas.

From selenite of silver values are presented from quantities, the greatest of which is ten times the least, the difference in the ratio obtained in these extremes being but slight. In the series obtained from ammonium selenium bromoselenate, the maximum quantity used is five times that of the minimum.

That the mean of the series from silver selenite approaches very closely the true atomic mass of selenium, can be little doubted. The values obtained in the reduction of silver chloride to metal express the commonly accepted ratio between silver and chlorine.

Selenium was shown to be completely removed from silver selenite by hydrochloric acid, and complete reduction of silver chloride to metal was proved in every instance. These facts

seem to afford good proof of the reliability of the hydrochloric acid method and the subsequent reduction process.

The advantages this method possesses over those used by previous workers is, first, the great reduction of the factor of personal error, in that the only part in which the operator is directly concerned is the weighing of material and product; second, the establishment, from one weight of starting material, of two values, whose mutual agreement depends on their similarity to a well-established ratio. The latter point indicates that the ratios prove themselves.

Additional evidence that the atomic mass of selenium is very close to the value given by the silver salt is furnished by the analysis of ammonium bromoselenate. This latter salt is easily obtained pure, and by decomposition with a reducing agent such as hydroxylamine, selenium itself can be weighed. In contrast to the previous method, the manipulation of the operator must needs play a great part, yet the satisfactory precipitation of selenium by hydroxylamine seems to be a strong point in its favor.

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## SECOND SECTION.

### INVESTIGATION OF THE DOUBLE BROMIDES.

Considerable attention has been drawn to the double bromides of tellurium by Wheeler.<sup>1</sup> Earlier work was done in the same line by Berzelius,<sup>2</sup> Rammelsberg,<sup>3</sup> and von Hauer.<sup>4</sup> Little was done on the corresponding derivatives of selenium, until Muthmann and Schäfer<sup>5</sup> prepared the double bromides of selenium with potassium and ammonium. The chlorides have received but little attention, and from what little has been done, they are known to be difficult to prepare. The double bromides are well-defined crystalline salts. The combination which takes place between selenium tetrabromide and certain of the alkaline bromides is so definite as to lead to the view that they are salts

<sup>1</sup> *Am. J. Sci.*, [3], 45, 267.

<sup>2</sup> *Pogg. Ann.*, 32, 577.

<sup>3</sup> *Ber. Monats. Ber.*, 1875, 379.

<sup>4</sup> *J. prakt. Chem.*, 73, 95.

<sup>5</sup> *Ber. d. chem. Ges.*, 26, 1008.



of hydrobromoselenic acid. Like the tellurium salts, they follow but one type,  $\text{Me}_2\text{SeBr}_2$ .

By examining these double salts, it was thought one or more might be found, which would answer the requirements of a starting material for the determination of the atomic mass of selenium. To this end a study has been made of the inorganic salts, and a number containing organic groups have also been prepared. Of all the salts examined, the most satisfactory one was the ammonium salt. The pyridine derivative appears as beautiful red scales, but the fact that it is only possible to obtain the salt from alcoholic solution, and that it is likely to suffer secondary decompositions, seemed to be an objection to its use in accurate analysis.

The method Muthmann and Schäfer employed in the preparation of the bromoselenates of potassium and ammonium was to treat selenium dioxide with hydrobromic acid, when a solution of selenium tetrabromide was formed. To this they added a saturated solution of potassium or ammonium bromide, and boiled. On cooling, a dark orange red powder separated, which contained octahedral crystals of bromoselenate.

A simpler and more convenient method of procedure was found to consist in adding bromine directly to a solution of the alkaline bromide, in which had been introduced the amount of selenium requisite to form the desired bromoselenate. The reactions took place in the following manner: Bromine coming in contact with selenium formed a dark layer of liquid monobromide, which being heavier than the solution, remained at the bottom of the vessel. Further addition of bromine converted the monobromide into tetrabromide, which reacting with the alkaline bromide present, formed bromoselenate. These reactions were all accompanied by evolution of heat. The excess of bromine was expelled on a water-bath, and on evaporation beautiful red crystals of bromoselenate separated. This method was found to be readily applicable in the preparation of inorganic bromoselenates.

In many double salts in which the ammonium group plays the part of alkaline metal, it is possible to replace the ammonia by an amine or aromatic base. In the case of platinum salts this takes place with ease, and subsequent experiments will

show that tetrabromide of selenium unites with the salts of the fatty amines and aromatic bases to form well-defined analogous salts.

In the preparation of the organic derivatives recourse must be had to another means of preparation, since bromine in free condition acts on the organic bodies themselves.

#### INORGANIC SALTS.

*Potassium Bromoselenate.*—This salt was prepared by the method above indicated, and was found to possess the same composition and properties as observed by Muthmann and Schäfer.

*Sodium and Lithium Salts.*—When the bromides of lithium and selenium or sodium and selenium are brought together, the mutual affinity is so small that no union occurs. On evaporating a solution of a mixture containing the respective salts, only alkaline bromide and selenious acid separated; neither exercise a sufficiently strong influence on the selenium to enable it to hold its bromine.

*Rubidium Bromoselenate.*—Pure rubidium bromide, tested spectroscopically and found to be free from cesium and potassium, was dissolved in water, selenium added, and bromine introduced. On evaporation at the low temperature of a water-bath, red crystals appeared, which examined under the microscope<sup>1</sup> showed the isometric combinations of cube and octahedron. In polarized light they proved to be isotropic.

On being subjected to analysis, the following data were obtained :

Salt. Gram.	Se. Gram.	Se. Per cent.
0.5015	0.0539	10.74
0.4999	0.0540	10.80
Salt. Gram.	AgBr. Gram.	Br. Per cent.
0.5012	0.7760	65.88

The formula  $\text{Rb}_2\text{SeBr}_4$  requires 10.82 per cent. Se and 65.72 per cent. Br.

The values used in calculation were :  $\text{Rb} = 85.43$ ,  $\text{Se} = 79.3$ ,  $\text{Br} = 79.95$ .

<sup>1</sup> The microscopic examinations were made with the assistance of Professor A. P. Brown, and to him the author is indebted.

*Cesium Bromoselenate.*—Cesium carbonate was dissolved in pure hydrobromic acid, and the resulting bromide crystallized. When examined with the spectroscope this salt showed absence of potassium and rubidium salts. On treatment of the salt with selenium tetrabromide, there appeared on evaporation crystals similar, in appearance and properties, to the salts of rubidium and potassium.

Analysis gave:

Salt. Gram.	Se. Gram.	Se. Per cent.
0.5009	0.0479	9.56
Salt. Gram.	AgBr. Gram.	Br. Per cent.
0.5007	0.6860	58.29

Calculated for  $\text{Cs}_2\text{SeBr}_6$ , 9.73 per cent. Se, 58.16 per cent. Br.  
 $\text{Cs} = 132.89$ ,  $\text{Se} = 79.3$ ,  $\text{Br} = 79.95$ .

These salts are all soluble in water to a colorless solution. With the rise of atomic mass of the basic element, the solubility decreases, the rubidium salt being less soluble in water than the potassium salt, while the cesium salt is rather insoluble. This property may be expected, since the alums, and particularly the chloroplatinates of these positive elements show a corresponding decrease in solubility as the atomic mass rises.

Attempts were made to prepare the bromoselenates of barium and cadmium, but like sodium and lithium, these salts do not appear to exist.

The salts of thallium, in the lower state of oxidation, in many cases closely resemble the alkali salts, such as in the formation of double platinum salts, etc. No bromoselenate seems to exist. Selenium tetrabromide, prepared from this dioxide and hydrobromic acid, and hence obtaining no free bromine, tends rather to oxidize thalious salts to the thallic state than to form double salts.

*Ammonium bromoselenate* was prepared in a manner similar to that of the salts of rubidium and cesium. It is less soluble in water than the potassium salt. Analysis indicated the composition  $(\text{NH}_4)_2\text{SeBr}_6$ . The crystals exhibit the same isometric combination of cube and octahedron that the salts of potassium, rubidium, and cesium show. The salt was considered to be

well adapted to accurate analysis, since ammonium bromide can be readily obtained pure both by sublimation and crystallization.

Analysis of the preceding salts was made by determining the bromine by precipitation with silver nitrate, in presence of sufficient free nitric acid to hold in solution the silver selenite which is simultaneously formed. The selenium was precipitated by hydroxylamine, and after washing with hot water, was brought upon an asbestos filter, dried at 100° and weighed.

#### ORGANIC SALTS.

For the preparation of the organic derivatives two methods were found to be available. The first consisted in preparing selenium tetrabromide by direct bromination of finely divided selenium, with the vapors of bromine. Red crystals of tetrabromide were formed, which are very soluble in alcohol to a red brown color. When a concentrated alcoholic solution of the amine salt is treated with a strong alcoholic solution of tetrabromide, a precipitate is produced which consists of bromoselenate of the amine. This precipitate was dissolved in alcohol containing hydrobromic acid, and the resulting colorless solution allowed to crystallize spontaneously. Crystallization can be greatly hastened by placing the solution in a desiccator containing soda-lime, and exhausting the air.

A second method employed and a more satisfactory one, was to treat selenium dioxide with concentrated hydrobromic acid. Alcohol was added to the solution to take up the excess of water. By treating the amine salt dissolved in alcohol with this tetrabromide, salts were obtained identical with those obtained by the former method. The latter method is by far the cleaner method and the one to be preferred.

As a rule, the organic salts in appearance closely resemble the alkaline salts; they generally consist of fine red powder. Water decomposes them, hence they cannot be crystallized from it. Prolonged action of ether, more rapidly when warm, extracts selenium bromide.

*Methylamine Bromoselenate.* — Methylamine hydrochloride, containing ammonium salts, was treated<sup>1</sup> with caustic soda and distilled; the vapors were collected in dilute sulphuric acid. The

<sup>1</sup> Fleck : This Journal, 18, 670.

neutral solution of mixed sulphates of ammonium and methylamine was evaporated to dryness, and the residue extracted with absolute alcohol. Ammonium sulphate remained insoluble, methylamine sulphate passing into solution. After filtration, the alcohol was evaporated, the sulphate treated with sodium hydrate, when methylamine was liberated in pure condition. The gas was collected in hydrobromic acid. This latter solution, on evaporation, yielded pure methylamine hydrobromide.

When methylamine bromide was treated in alcoholic solution with selenium tetrabromide, a red precipitate formed, which on recrystallization from alcohol containing hydrobromic acid, gave a very finely crystalline body, which analyzed as follows :

Salt. Grams.	Se. Gram.	Se. Per cent.
1.0067	0.1266	12.57
Salt. Gram.	AgBr. Grams.	Br. Per cent.
0.9874	1.7829	76.83

The formula  $(\text{CH}_3\text{NH}_2)_2\text{SeBr}_2$  requires Se 12.72 per cent. and Br 76.96 per cent. The values used in calculation were : H = 1.008, C = 12.01, N = 14.04, Se = 79.3, Br = 79.95.

*Ethylamine Bromoselenate.*—This salt was prepared from ethylamine bromide and selenium tetrabromide in a manner similar to the salt of methylamine. It forms flat hexagonal prisms, red in color. Analysis gave :

Salt. Grams.	Se. Gram.	Se. Per cent.
1.0008	0.1215	12.14
Salt. Gram.	AgBr. Gram.	Br. Per cent.
0.5619	0.9713	73.55

The formula  $(\text{C}_2\text{H}_5\text{NH}_2)_2\text{SeBr}_2$  requires Se 12.17 per cent. and Br 73.66 per cent.

*Dimethylamine Bromoselenate.*—Dimethylamine was prepared by boiling nitroso-dimethylaniline with caustic soda ; quinone oxime was formed, while at the same time dimethylamine was evolved as a gas, and collected in dilute acid. A good yield was obtained by this method. The salt obtained was again distilled with sodium hydroxide and the gas absorbed in dilute

hydrobromic acid. After crystallization the bromide was dissolved in alcohol and treated with selenium tetrabromide. On allowing the alcoholic solution to evaporate, red crystals were obtained, similar in appearance to the salt of methylamine.

Analysis gave :

Salt. Grams.	Se. Gram.	Se. Per cent.
1.0233	0.1251	12.22
Salt. Gram.	AgBr. Gram.	Br. Per cent.
0.5227	0.9049	73.66

$[(CH_3)_3NH]_2SeBr_4$  is an isomeride of ethylamine bromoselenate and like it requires Se 12.16 per cent. and Br 73.66 per cent.

*Trimethylamine Bromoselenate.*—Trimethylamine was freed from contaminating ammonium salts, by treatment of the mixed sulphates with absolute alcohol, when the amine salt dissolves, leaving ammonium sulphate insoluble. Trimethylamine was liberated by treatment of the sulphate with caustic soda and absorbing the free amine in hydrobromic acid. The bromoselenate was prepared by adding a solution of selenium tetrabromide to trimethylamine bromide, dissolved in alcohol. The red precipitate formed was recrystallized from alcohol, when a fine red crystalline powder was obtained.

Analysis gave :

Salt. Grams.	Se. Gram.	Se. Per cent.
1.0010	0.1195	11.93
Salt. Grams.	AgBr. Grams.	Br. Per cent.
1.0501	1.7406	70.53

A determination of nitrogen by the Kjeldahl method gave 4.18 per cent. N. The formula  $[(CH_3)_3NH]_2SeBr_4$  requires Se 11.68 per cent., Br 70.62 per cent., and N 4.13 per cent.

*Tetraethyl Ammonium Bromoselenate.*—The bromide was prepared by treating the base with hydrobromic acid. The bromoselenate was prepared in the same manner as previously described salts and crystallizes from alcoholic solution in minute flat hexagonal plates.

Analysis gave :

Salt. Grams.	Se. Gram.	Se. Per cent.
1.0021	0.0991	9.89
Salt. Gram.	AgBr. Gram.	Br. Per cent.
0.5366	0.7391	58.60

The formula  $[(C_6H_5)_3N]_2SeBr_4$  requires Se 9.67 per cent. and Br 58.53 per cent.

It thus appears that all of the hydrogen atoms in ammonium bromoselenate can be replaced by a fatty amine. An entirely different behavior is shown by the aromatic amines. Aniline hydrobromide in hydrobromic acid solution precipitates selenium completely from a solution of selenium tetrabromide.

When an alcoholic or aqueous solution of selenium tetrabromide is treated with hydrobromide of aniline and filtered, the filtrate is found to be free from selenium, showing complete precipitation has taken place.

As might be expected from this behavior of aniline, diphenylamine in hydrobromic acid solution forms no derivative with selenium tetrabromide.

In the many reactions that were tried with phenylhydrazine, it appears that this substance seems to be almost as good a reagent for the precipitation of selenium as hydroxylamine.

*Pyridine Bromoselenate.*—Both pyridine and quinoline are strongly basic bodies of the aromatic series; the first forms a well-defined bromoselenate, while the second forms a compound which decomposes so readily with the separation of selenium that it is impossible to analyze it.

On treating pyridine hydrobromide in alcoholic solution with selenium tetrabromide, a crystalline precipitate is produced, which, recrystallized from alcohol, forms beautiful deep red scales. Under certain conditions it is possible to obtain the salt as prismatic crystals. This salt, like the salts of the fatty amines, dissolves in water to a colorless solution. Water, benzene, chloroform, ether, and carbon bisulphide dissolve in salt, but on evaporation of the solvent decomposition takes place, selenium separating. It has only been possible to obtain the salt from alcoholic solution.

A complete analysis was made; carbon and hydrogen were

determined by combustion. Nitrogen was determined by the method of Dumas.

Salt. Grams.	Se. Gram.	Se. Per cent.
1.0011	0.1121	11.19
Salt. Grams.	AgBr. Grams.	Br. Per cent.
0.5007	0.7846	66.63
1.0057	1.5769	66.71
Salt. Gram.	H <sub>2</sub> O. Gram.	H. Per cent.
0.4006	0.0645	1.79
Salt. Gram.	CO <sub>2</sub> . Gram.	C. Per cent.
0.4006	0.2465	16.75

0.5151 gram of the salt gave 17 cc. of nitrogen, equivalent to 4.14 per cent.

The formula  $(C_5H_5NH)_2SeBr_4$  requires H 1.67 per cent., N 3.90 per cent., Se 11.02 per cent., C 16.74 per cent., and Br 66.69 per cent.

Unless a slight excess of selenium tetrabromide is present in the solution undergoing crystallization, the salt dissociates to a slight degree. This fact and the tendency it showed to lose bromine, when dried over soda-lime, seem to be serious objections to its employment in an atomic mass determination.

*Piperidine Bromoselenate.*—Like pyridine, piperidine yields a strongly crystalline body with selenium tetrabromide. The salt was prepared in a manner similar to that of the pyridine salt. When crystallized from alcohol red tabular crystals appeared.

Analysis gave:

Salt. Gram.	Se. Gram.	Se. Per cent.
0.5002	0.0540	10.79
Salt. Gram.	AgBr. Gram.	Br. Per cent.
0.5305	0.8161	65.46
Salt. Gram.	CO <sub>2</sub> . Gram.	C. Per cent.
0.4004	0.2422	16.49
Salt. Gram.	H <sub>2</sub> O. Gram.	H. Per cent.
0.4004	0.1369	3.52

The formula  $(C_5H_{11}NH)_2SeBr_4$  requires H 3.30 per cent., N



3.84 per cent., Se 10.84 per cent., C 16.46 per cent., and Br 65.59 per cent.

On standing over soda-lime, this salt, like the pyridine compound, slowly loses bromine.

When the mother-liquor from which the red soluble crystals were obtained was allowed to slowly evaporate, a black salt appeared, from which, when treated with water, large quantities of selenium immediately separated. Analysis of various samples of this black compound gave determinations of selenium from 11.79–14.39 per cent. Bromine estimations indicated a variation in content from 67.42 per cent. to 70.71 per cent. From the irregularities in composition of different samples and the variations in color from red to black, it would appear that piperidine bromoselenate, when crystallized from solutions containing an excess of selenium tetrabromide, tends to enclose the latter and carry it down with it.

### THIRD SECTION.

#### SELENIUM MONOXIDE.

Different chemists at various times have either affirmed or denied the existence of the monoxide of selenium. Berzelius ascribes the odor of rotten horseradish, noticed when selenium burns in air, to the existence of this oxide. Chabrie,<sup>1</sup> in his work on the organic derivatives of selenium, claims to have prepared the monoxide by heating selenium to 180° in air. So firmly convinced was he that the monoxide exists that he used this method as a means of estimating selenium. A. W. Pierce<sup>2</sup> has made an investigation of Chabrie's work, and concludes that it is probably not formed by the method of Chabrie, and thinks the odor produced when selenium is burned in air is due to the presence of moisture, which, under the circumstances, would produce hydrogen selenide.

While subliming the large quantities of pure dioxide used in the preceding investigation, at no time was there noticed an odor like that produced when selenium burns in air or when a selenide is roasted. On the contrary, the vapor of selenium

<sup>1</sup> *Ann. chim. phys.* [6], 20, 273.

<sup>2</sup> *Ztschr. anorg. Chem.*, 13, 121.

dioxide which at times escaped into the air, gave an odor much resembling that of sulphur trioxide.

An experiment was made to determine whether selenium would reduce the dioxide when heated in an open vessel at the atmospheric pressure. No combination was found to take place.

A second experiment was made, in which equivalent parts by weight of selenium and dioxide were placed in a stout glass tube of hard glass, about forty inches long by one-half inch internal diameter. The tube was sealed and heated in a large flame, until the selenium melted. The dioxide under the pressure generated by its own volatilization, melted to a thick liquid. The temperature was raised to the boiling-point of selenium. Should selenium be able to reduce the dioxide, it should do so in a solution of the combined gases. Such, however, is not the case; on cooling, the mass resolves itself into separate layers of selenium and dioxide. When the tube was opened, no pressure was observed (such as would have been the case had a gas been formed), nor could any odor be detected. On treating the mass with water, selenious acid was formed, which dissolved, leaving selenium insoluble.

Selenium and tellurium have many derivatives from which well-established analogies can be drawn. Where a derivative of one element exists, a corresponding derivative of the other is usually found. That tellurium forms a monoxide, there can be little doubt, hence it has seemed probable that a monoxide of selenium should exist. However, in considering their halides, we find that while tellurium forms the compounds  $\text{TeX}_2$  and  $\text{TeX}_4$ , directly analogous to the oxides  $\text{TeO}$  and  $\text{TeO}_2$ , selenium forms only those halides of the types  $\text{Se}_2\text{X}_4$  and  $\text{SeX}_4$ , the latter corresponding to the well-known  $\text{SeO}_2$ . From the analogy thus established between the oxygen and halogen derivatives, one would rather expect an oxide  $\text{Se}_2\text{O}$  than  $\text{SeO}$ . It was therefore thought that the lower oxide might be prepared by treatment of the monobromide with dry silver oxide.  $\text{Se}_2\text{Br}_4$  was prepared by rubbing the tetrabromide with selenium. No action could be brought to take place between silver oxide and a solution of the bromide in carbon disulphide. When the liquid bromide is treated at the ordinary temperature with silver oxide, a violent reaction takes place. Much heat is evolved, the reaction being

explosive in character. The resulting mass on treatment with water gives a solution containing only selenious acid.

If the monoxide is formed it is likely that the heat of the reaction would decompose it. The experiment was subsequently modified by chilling the bromide to  $-7^{\circ}$ . At this temperature, silver oxide swims unattacked on the surface of the liquid monobromide. No reaction takes place until the whole attains a temperature of  $+20^{\circ}$ , when the same violent reaction takes place that was before noted. On conducting the experiment in a closed tube, it is noticed that on opening the tube, no pressure exists, hence it is unlikely that a gas has been formed. Should a lower oxide be formed at all in this reaction, the experiments seem to indicate that it immediately dissociates into selenium and the dioxide.

As Pierce has pointed out, it seems very likely that the odor noticed when selenium is roasted in air, is due to the presence of hydrogen selenide, and that efforts to obtain other oxides than the dioxide, thus far have been unsuccessful.

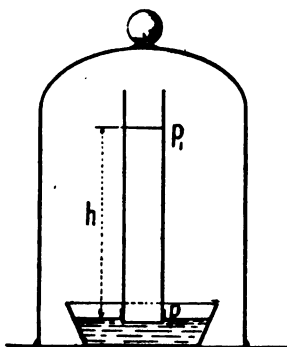
UNIVERSITY OF PENNSYLVANIA.

## OSMOTIC PRESSURE.

BY C. L. SPEYERS.

Received May 26, 1898.

CONSIDER the following arrangement: The lower vessel contains pure solvent; the tube contains a solution of some non-volatile body in that solvent. The tube is open at the



top but closed at the bottom by a diaphragm permeable to the solvent only. At equilibrium, the arrangement is to be so

adjusted that the diaphragm is just at the surface of the solvent in the outer vessel. The tube and vessel holding the solvent are covered by a bell jar, the air being removed so that the only aeriform body under the bell jar is the vapor of the solvent. This is the arrangement described by Arrhenius.<sup>1</sup> At equilibrium, the counter pressure preventing the entrance of the solvent, is commonly given as equal to  $hs$  on the unit surface,  $h$  being the height of the column of liquid and  $s$  the density of the solution whose counter pressure balances the osmotic pressure,  $\pi$ , so that at equilibrium

$$\pi = hs \dots \dots \dots (1)$$

The difference between the pressure of the vapor on the top of the solution and the pressure of the vapor on the pure solvent in the lower vessel is so slight compared with  $\pi$  that for our purpose it is negligible. Likewise the coefficient of compressibility of solvent may be neglected by us.

The value of  $h$  is *a priori* unknown, but when the system reaches equilibrium, then  $h$  must have such a value that the vapor-pressure of the solution equals the vapor-pressure of the pure solvent at height  $h$ .

Now

$$dp = -s'dh$$

where  $s'$  is the density of the vapor compared with hydrogen.

Experiments by Ramsay and Young, quoted by Noyes and Abbot,<sup>2</sup> show that the density of ether vapor at  $12.9^\circ$  and under pressure  $p$  in terms of hydrogen at the same temperature and under the same pressure is  $36.08 + 0.0581p$ . One cc. hydrogen at  $12.9^\circ$  and under  $p$  pressure weighs  $(0.0,8987p/76)$   $273/283.9$  grams.

$$s' = 0.0,8987 \frac{p}{76} \cdot \frac{273}{283.9} (36.08 + 0.0581p) \text{ grams.}$$

Wherefore, for ether as solvent,

$$h = \frac{76 \cdot 285.9}{0.0,8987 \cdot 273} \int_{p_1}^{p_0} \frac{dp}{p(36.08 + 0.0581p)} \text{ cm.}$$

<sup>1</sup> *Ztschr. phys. Chem.*, 3, 115 (1889).

<sup>2</sup> *Ibid.*, 23, 56 (1897).

Integrating by partial fractions, we get

$$h = 24540 \log \frac{p_0(36.08 + 0.0581p_1)}{p_1(36.08 + 0.0581p_0)} \text{ cm.}$$

Substituting in 1 we get

$$\pi = 24540 \cdot 13.60 s \log \frac{p_0(36.08 + 0.0581p_1)}{p_1(36.08 + 0.0581p_0)} \text{ in grams} \dots (2)$$

The next step is to substitute for  $s$ , which in this case is to refer to ether.

Now this little paper centers around this quantity  $s$ . I wish to show that for  $s$  we should substitute the value for the pure solvent, in this case ether, and not the value for the solution which is in the tube at the time of consideration. This latter value was used by Arrhenius.<sup>1</sup>

Does not the great advantage of the modern theory of solution lie in the notion that the constituents of a liquid homogeneous mixture, are independent of each other? Is not this far more suggestive than the assumption of a peculiar, characteristic, almost chemical, action between the constituents, which assumption even the originators of the modern theory of solution seem at times inclined to make? For when the constituents are independent of each other, then we must seek the apparently peculiar characteristic action of one constituent upon the other constituent of a homogeneous liquid mixture, in a difference of condition offered by the one constituent to the other. For instance, suppose we have ammonium chlorid in the form of partially dissociated vapor and we introduce some nitrogen, keeping temperature and total pressure constant. Then the ammonium chloride is believed to dissociate still more; but not because the nitrogen acts chemically upon this system or in any other characteristic way upon it. Not at all. But because the introduction of nitrogen necessitates a change in the condition of the system. Of course the change in condition in this case is readily detected, whereas the changes in condition produced when one of the constituents of a homogeneous liquid mixture is changed are not so easily followed up. Nevertheless, it would seem more profitable to seek for the cause of apparently specific

<sup>1</sup> *Loc. cit*

action in this direction rather than in the direction of chemical affinity or chemical action; the latter notion is so vague.

Granting this independence of the constituents, the notion of a diaphragm permeable to one constituent but not to the other, becomes clear enough.

In the arrangement considered above, the diaphragm is permeable to the constituent present in larger quantities and therefore generally called the solvent. In this case ether is the solvent. As the diaphragm is impermeable to the solute, should we not claim that it receives the full pressure of the solute, not allowing any activity on the part of the solute to pass through the diaphragm? How can we claim anything else? But then when we do this, how can we claim that the hydrostatic pressure preventing the entrance of the ether, comes from anything else than the column of pure ether in the solution, which column of pure ether has the height of the column of solution? We cannot, consistently, with what we have assumed regarding the independence of the constituents of the liquid mixture. For we are not to look upon a molecule of ether locked to a molecule of solute, so that whither the ether molecule goes, the other molecule must go. Not at all, not even for an instant. And yet, how can we mean otherwise when we say that  $s$  in equation (1) shall refer to the solution as a whole and not to the solvent in it.

Now in the paper of Noyes and Abbot<sup>1</sup> from which paper the above calculations have been taken, there is a collection of data which will be useful in testing this view.

In that paper they describe an arrangement which we must look upon as purely imaginary; the arrangement cannot be looked upon as possible in fact, though perhaps interesting from a theoretical point of view. Instead of putting the diaphragm at the bottom of the tube, they put it at the top of it and assume that the pure solvent rises in the tube until its hydrostatic pressure balances the osmotic pressure of the solute. But in their development of the necessary formulas, they do not take into account the external air pressure needed to force up the column of liquid supposing the arrangement to be subject to the air-pressure, or if in a partial vacuum such as we have assumed in our arrangement, they do not show how such a column of

<sup>1</sup> *Loc. cit.*

liquid could possibly rise in the tube, for the difference in pressure,  $p_0 - p_1$ , is insignificant compared with  $\pi$ . In either case, so far as their results depend upon their theoretical deductions, they are valueless, but considered by themselves, the data are very valuable, and will serve us a good turn.

Substituting in (2) the value for  $s$  for pure ether, given by Noyes and Abbott, equal to 0.7206, and passing to Briggs' logarithms, we get

$$\pi = 553900 \left( \log \frac{63.08 - 0.0581 p_1}{p_1} - 0.0607 \right) \dots\dots (3)$$

On the other hand, knowing the concentration, we can calculate  $\pi$  by Avogadro's law. The two values should agree. In the following table, largely from Noyes and Abbot,  $c$  is the quantity of solute, in one series naphthalene, in the other azobenzene, in one part of ether at 12.9°,  $p$  is the vapor-pressure of the solution in cm. of mercury,  $s$  is its density,  $\pi_1$  is the osmotic pressure calculated from (3),  $\pi_0$  is the osmotic pressure calculated from (3) but substituting the density of the solution for the density of the pure solvent,  $\pi_0$  is the osmotic pressure calculated according to Avogadro's law,  $\Delta\pi_1$  is the percentage variation of  $\pi_1$ , compared with  $\pi_0$  as the standard,  $\Delta\pi_0$  is the percentage variation of  $\pi_0$ , compared with  $\pi_0$  as the standard.





Judging from these figures, there can hardly be any question that the density of the solvent and not that of the solution is to be used in computing  $\pi$  by the hydrostatic method.

RUTGERS COLLEGE, May, 1898.

### METHOD OF PREPARING A STRICTLY NEUTRAL AMMONIUM CITRATE SOLUTION.

By A. D. COOK.

Received June 8, 1898.

FOR the benefit of many analytical chemists who are engaged in fertilizer work and for the purpose of securing uniformity in results, I respectfully submit the following pertaining to the neutrality and preparation of the chemical reagent "ammonium citrate."

This reagent has caused more trouble than all the other reagents required in fertilizer work, and yet it is an extremely easy matter to get a strictly neutral reaction.

The method adopted by the Association of Official Agricultural Chemists does not state the most essential fact in the preparation of this reagent, and the one which, if universally adopted, would overcome many obstacles in its preparation.

The failure to obtain a strictly neutral solution of ammonium citrate has caused great discrepancy in results among chemists who have analyzed the same material. I refer more particularly to the analysis of concentrated phosphates where there is a large per cent. of available phosphoric acid. The total phosphoric acid running as high as fifty per cent., the insoluble eleven per cent., making the available thirty-nine per cent. In the chemical laboratory at this station, where from 800 to 1000 samples of commercial fertilizers are analyzed annually, I have had ample opportunity to try different methods and to compare results obtained by chemists working with different solutions of ammonium citrate. It has been pointed out by fellow-workers in this field that a strictly neutral solution may be obtained by allowing the solution to stand after ammonia has been added to the citric acid and the proper dilution made. I have found that the practicability of this procedure depends upon the temperature of the solution. If vigorous stirring is neglected the solution will be slightly alkaline. Vigorous stirring, thus causing

heat by chemical action, will generate sufficient heat to drive off the excess of ammonia, and this is the main point to observe in securing its neutrality.

This reagent is made up as follows in this laboratory: 740 grams of commercial citric acid are carefully weighed out and placed in a four-liter graduate containing 1900 cc. of ten per cent. ammonium hydroxide. With a suitable glass rod the citric acid is thoroughly and vigorously stirred until the citric acid has all dissolved. Distilled water is now added until the meniscus reads 4000 cc. The solution is again stirred and carefully transferred to a large porcelain evaporating dish. The solution is allowed to stand over night and in the morning large oval crystals are noticeable on the sides of the four-liter graduate, and invariably the solution when tested for neutrality will be found strictly neutral. If the solution is not vigorously stirred sufficient heat will not be evolved to drive off the excess of ammonia, and when tested will be found to be slightly alkaline, but by resorting to vigorous stirring, a strictly neutral reaction will be obtained. The solution, after being transferred to the reagent bottle, is brought to the required temperature, 20° C., and distilled water added until the specific gravity is 1.09. On testing the neutrality of this solution, both with coralline and cochineal as indicators, it will be found unnecessary to alter its neutrality in the least degree, the solution being strictly neutral.

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### THE ASSAY OF TELLURIDE ORES.

BY CHARLES H. FULTON.

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THE growing importance of telluride ores and the fact of their relative difficulty of assay in contrast with other ores, has led to this work. The object of the work was to determine where the difficulty and losses lay, and if possible to remedy these defects of the assay by proper methods and precautions.

*Ore No. 1* is a telluride ore, having a gangue, mainly of quartz. A very small amount of pyrite is also present.

*Ore No. 2* is a very rich telluride from Cripple Creek, Colorado, containing considerable pyrite. The gangue is siliceous.

Both ores were finely crushed, No. 1 crushed to 100-mesh, and No. 2 to 150-mesh, to insure an even sample. The crucible assay was tried on these ores with various modifications of the charge as regards the amount of litharge present. All assays on ore No. 1 were made on one assay ton of ore. The assays on ore No. 2 were made on one-fifth assay ton.

The charges for ore No. 1 were as follows, except that the litharge increased from one assay ton to six assay tons in the series :

- 1 assay ton ore.
- 1 assay ton litharge.
- $\frac{1}{2}$  assay ton silica.
- 1 assay ton soda.
- 10 grams borax glass.
- 2 grams argol.
- Salt cover.

The amount of silver in the ore is very small, and was disregarded in the assays. Twenty milligrams of silver foil were added to each crucible assay to give a larger button in cupellation and to avoid subsequent inquartation. Four iron nails were also added to each assay to desulphurize and give a malleable button.

The lead buttons ranged in weight from twenty to forty-eight grams, the increase in weight being due to the increasing litharge. All buttons were fairly malleable and were cupelled directly, even the larger buttons, without previous rescorification. The cupellation was conducted at a low heat, with feathers of litharge.

The assays show a regular increase of gold as the litharge increases, with the exception of B and B<sub>2</sub> and ranged from 5.60 milligrams to 5.78 milligrams. A further increase of litharge showed no better result. (See Table I.)

The slags from these crucible assays were ground up and mixed with one assay ton of litharge and two grams of argol, and fused. The resulting lead button was cupelled with the addition of ten milligrams of silver to give a button which could be parted.

The results of correction of the crucible assay show that con-

TABLE I.—SHOWING EFFECT OF INCREASING LITHARGE. ORE NO. I.

Number of assay.	Amount of litharge	Amount of argol.	Character of slag.	Character of lead button.	Weight of lead button.	Amount of gold.		Gold recovered from crucible slag.		Gold recovered from cupel.		Total amount of gold recovered.	Percentage recovered from crucible slag.		Percentage recovered from cupel.	Total percentage recovered.	Amount of gold in corrected assay.
						Grams.	Milli-grams.	Milli-gram.	Milli-gram.	Milli-gram.	Per cent.		Per cent.	Per cent.			
A	1	2	black glassy	malleable	20	5.60	0.03	0.09	0.12	0.52	0.55	0.18	2.07	0.55	0.18	2.07	5.72
B	2	2	"	brittle	37	5.52	0.16	0.02	0.18	2.76	0.18	0.04	2.94	0.18	0.18	2.94	5.70
B <sub>0</sub>	2	2	"	"	47	5.69	0.03	0.01	0.06	0.52	0.09	0.06	0.61	0.09	0.09	0.61	5.64
C	4	2	green glassy	"	32	5.67	0.05	0.01	0.10	0.86	0.09	0.10	0.95	0.09	0.18	0.95	5.73
C <sub>0</sub>	4	2	"	"	30	5.65	0.08	0.02	0.07	1.38	0.18	0.07	1.56	0.18	0.18	1.56	5.75
D	6	2	"	malleable	48	5.72	0.06	0.01	0.07	1.03	0.09	0.07	1.12	0.09	0.09	1.12	5.79
D <sub>0</sub>	6	2	"	"	45	5.78	0.06	0.01	0.07	1.03	0.09	0.07	1.12	0.09	0.09	1.12	5.85
Averages,						5.65	0.068	0.013	0.09	1.16	0.12	0.09	1.48	0.12	0.12	1.48	5.74

These assays were run with iron nails to desulphurize.

siderable gold is retained in the slag. The assays which contain the least amount of litharge retain the most gold. The average correction was 0.068 milligram, which is equivalent to 1.16 per cent. The highest corrected assay was taken as 100. This loss of gold in the crucible slag is much greater than that in ordinary ore assays.

The cupels were also ground up and mixed with one assay ton of litharge, one and a half assay tons of borax glass, one assay ton of soda, and two grams of argol. Silver was added to the fusion.

The amount of gold recovered from the cupel is small, only 0.013 milligram, equivalent to 0.12 per cent.

It is also to be noted that the corrected assays increase with the greater quantity of litharge, as well as the uncorrected assays, which shows that part of the loss is due to volatilization.

Table II shows the effect of increasing the litharge on a rich telluride. The charges for this ore were as follows, except as before, for the varying litharge: One-fifth assay ton ore, two assay tons litharge, one assay ton soda, one gram argol. The ore had considerable reducing power, and one gram of argol was found to be sufficient to give the right-sized button.

The crucible slags were remelted and the resulting lead buttons cupelled. The actual loss of gold in slags for this ore was higher than for No. 1, although the percentage loss decreases. The loss in the cupel being small, it was neglected in this case. The silver contents of this ore were determined, but no correction for the loss of silver in slags and cupels was made.

When the button resulting from the fusion of a telluride ore was brittle, it was usually deemed necessary to rescorify it before cupellation. The button resulting from telluride fusions is usually brittle and scorification is almost always resorted to. A set of assays were run on ores No. 1 and No. 2 to determine whether this is of advantage. These sets were run, as the previous ones, with increasing litharge, but no nails were added to desulphurize. All the buttons were rescorified, some with the addition of test-lead.

Tables III and IV show the results of these sets. The gold is considerably lower when the buttons are rescorified, and also it is evident that the loss takes place during the scorification.

TABLE II.—SHOWING EFFECT OF INCREASING LITHARGE ON A RICH TELLURIDE. ORE NO. 2.

Number of assay.	Amount of lith- arge.	Amount of ore.	Amount of argol.	Character of slag.	Character of lead button.	Weight of lead button.	Amount of gold.	Gold recovered from crucible slag.	Per cent. recovered from crucible slag.	Amount of gold in corrected assay.
	Assay tons.	Assay ton.	Gram.			Grams.	Milli- grams.	Milli- gram.	Per cent.	Milli- grams.
1	2	1	1	green glassy	fairly malleable	20	89.10	0.22	1.21	90.20
2	4	1	1	" "	" "	26	90.50	0.08	0.31	90.90
3	4	1	1	" "	" "	48	90.26	0.10	0.55	90.36
4	6	1	1	" "	malleable	28	90.30	0.09	0.49	90.75
					Averages,		90.04	0.09	0.45	90.55

TABLE III.—SHOWING EFFECT OF RESCORIFICATION OF LEAD BUTTON. ORE NO. I.

Number of assay.	Amount of litharge.	Weight of lead button.	Weight after rescorification.	Amount of gold.	Gold recovered		Gold recovered from scorification		Gold recovered from cupel.	Total amount of gold recovered.	Percentage recovered from crucible slag.		Percentage recovered from scorification slag.	Percentage recovered from cupel.	Total percentage recovered.	Amount of gold in corrected assay.
					Milli-gram.	Milli-gram.	Milli-gram.	Milli-gram.			Per cent.	Per cent.				
E.	1	17	8	5.32	0.10	0.16	0.04	0.01	0.11	0.26	1.72	2.76	0.18	4.84	5.58	
F.	2	22	14	5.62	0.06	0.04	0.04	0.01	0.11	0.11	1.03	0.70	0.18	1.91	5.73	
G.	4	30	18	5.64	0.06	0.04	0.04	0.01	0.11	0.11	1.03	0.70	0.18	1.91	5.75	
H.	6	40	14	5.50	0.08	0.05	0.05	0.04	0.11	0.11	1.38	0.52	0.18	1.90	5.61	
H <sub>0</sub>	6	39	14	5.54	0.09	0.04	0.04	0.04	0.13	0.13	1.55	0.70	0.18	2.20	5.67	
I.	8	75	24	5.58	0.07	0.04	0.04	0.04	0.11	0.11	1.20	0.65	0.18	2.20	5.65	
Averages,				5.54	0.08	0.038	0.04	0.04	0.11	0.11	1.31	0.65	0.18	1.98	5.77	

TABLE IV.—SHOWING EFFECT OF RESCORIFICATION OF LEAD BUTTON, RICH TELLURIDE. ORE No. 2.

Number of assay.	Amount of lith- arge.	Amount of ore.	Amount of argol.	Character of lead button.	Weight of lead button.	Weight after re- scorification.	Amount of gold.	Gold recovered from crux slag.	Corrected assay.
	Assay tons.	Assay ton.			Grams.	Grams.	Milligrams.	Milligram.	Milligrams.
10	4	1	none	malleable	68	29	89.30	....	....
11	4	1	"	"	54	26	89.60	....	....
12	6	1	"	"	76	24	88.50	0.20	88.70
					Averages,		89.13		

These assays were run with niter and iron nails to desulphurize.



This loss is partly in the scorification slag and partly by volatilization. The crucible slags, cupels, and scorification slags were remelted and the buttons cupelled. The loss in the crucible slag is a little higher than in the first set (Table I).

The average amount of gold recovered from the scorification slag is 0.038 milligram, equivalent to 0.65 per cent. The amount recovered from the cupel is very small and less than in Table I.

The assays run on the rich telluride, with rescorification, point to the same conclusion (Table IV). This set of assays was run with niter and iron nails to increase the oxidizing action and to desulphurize. This loss of gold during rescorification is much greater in tellurides than in ordinary ores. With the latter it usually amounts to no more than a trace. The average result, by direct cupellation, is always higher than that obtained when the buttons are first rescorified.

A charge with potassium cyanide was run on ore No. 1. Ore, one assay ton; potassium cyanide, two assay tons; litharge, one assay ton; salt cover and silver. This gave gold 5.40, which is much lower than the results of assays run by the ordinary charges.

The following are the average results obtained from the four sets of assays :

ORE NO. 1.

Average uncorrected assay, when cupelled directly, 5.65 milligrams.

Average corrected assay, when cupelled directly, 5.74 milligrams.

Average uncorrected assay, when button is rescorified, 5.54 milligrams.

Average corrected assay, when button is rescorified, 5.67 milligrams.

Average loss of gold in crucible slag, 0.075 milligram.

Average loss of gold in per cent., 1.23 per cent.

Average loss in cupel, when cupelled directly, 0.013 milligram.

Average loss in cupel, in per cent., 0.12 per cent.

Average loss in scorification slag, 0.038 milligram.

Average loss in per cent., 0.65 per cent.

Total gold recovered when cupelled directly, 0.09 milligram.

Total gold recovered in per cent., 1.48 per cent.

Total gold recovered when rescorified, 0.11 milligram.

Total gold recovered in per cent., 1.98 per cent.

#### ORE NO. 2.

Average uncorrected assay, cupelled directly, 90.04 milligrams.

Average corrected assay, cupelled directly, 90.55 milligrams.

Average uncorrected assay, when rescorified, 89.13 milligrams.

Average loss of gold in crucible slag, 0.09 milligram.

Average loss of gold in per cent., 0.45 per cent.

A set of assays was also run in which the heat of the fire and time in fire was varied, to determine whether these factors had any influence on the result obtained. The fires were varied from a red to a white heat and the time from thirty minutes to one hour. The difference in results was not appreciable, and a good, moderately hot fire, with from forty to fifty minutes in the furnace, gave the best results. Cupellation, however, should be carried on at a low heat.

#### SCORIFICATION ASSAYS.

Both ores, Nos. 1 and 2, were run by scorification with very variable results, but uniformly lower than the crucible assay.

Ore No. 1 was assayed by the following charge :

Ore, one-fifth assay ton.

Test-lead, seventy grams.

Borax glass, one-half gram.

Litharge cover, twenty grams.

This gave gold = 4.30 milligrams. (Crucible assay ran 5.62 milligrams.) In the next charge the test-lead was increased to eighty grams. Otherwise charge was the same.

This gave gold = 4.80 ounces.

Then to further increase the ratio of ore to test-lead these charges were run in duplicate.

## No. 1.

Ore, one-tenth assay ton.

Test-lead, fifty grams.

Borax glass, one-half gram.

Litharge cover, twenty grams.

## No. 2.

Ore, one-tenth assay ton.

Test-lead, sixty grams.

Borax glass, one-half gram.

Litharge cover, twenty grams.

No. 1 gave gold, 4.20 and 4.00 milligrams, respectively.

No. 2 gave gold, 5.00 and 5.40 milligrams, respectively.

The heat was kept low throughout.

More assays were run by various charges, but invariably gave low results. A great drawback to the method is the large amount of test-lead which must be used, giving a button too large to be cupelled easily. The litharge cover seems of advantage, but also tends to increase the size of the lead button by protecting the lead from scorification.

Ore No. 2 was run by the following charge :

Ore, one-tenth assay ton.

Test-lead, fifty grams.

Litharge cover, twenty grams.

Borax glass, one-half gram.

This gave gold, 74.80 ounces (crucible assay, 90.20 ounces).

The test-lead was increased to sixty grams, giving 78.70 milligrams gold.

The scorification slags were ground up and assayed :

No. 1 gave 0.42 milligram = five and six-tenths per cent. of gold.

No. 1 gave 0.38 milligram gold.

This makes corrected result per assay ton on No. 1 = 79.0 milligrams.

This makes corrected result per assay ton on No. 2 = 81.8 milligrams.

This shows the corrected assay by scorification still away below the ordinary crucible assay. The loss of gold in scorification slag is very great, but evidently a still greater loss takes place by volatilization.

These results readily show that the crucible assay is much the better for telluride ores.

## CONCLUSIONS.

It is very evident that a large excess of litharge is necessary to obtain good results in assaying a telluride ore. The amount of litharge will vary with the richness of the ore, the proper proportion of litharge to ore being maintained in a rich telluride by decreasing the quantity of ore. A definite ratio of litharge to gold present in telluride ores might be established.

The loss of gold in the crucible slag is many times more than that in assaying ordinary ores, and with both low and high grade ores justifies the making of corrected assays where accuracy is required. The loss of gold by absorption in the cupel is not of much account.

Scorification of any kind is bad for a telluride ore, whether it be the direct scorification of the ore or the rescorification of brittle or large buttons.

The loss in cupelling a large or brittle button directly is much less than if it were first rescorified.

The amount of gold lost in the scorification slag when scorifying the ore directly is very great, amounting to five and six-tenths per cent.

The highest uncorrected result also gives the highest corrected result, showing that loss takes place by volatilization. The loss of gold in a rich telluride is greater than in a low grade ore, but the percentage loss decreases with the richness of the ore.

In general, the crucible assay is best by far for telluride ores. The fire should be moderately hot, the length of time from forty to fifty minutes. The assay should be so conducted as to give a button of good size, from twenty to twenty-eight grams, which can be cupelled directly. The cupellation should be done at a low heat with crystals of litharge forming on the cupel. When the assay is to be accurate, the crucible slag should be remelted and the first result corrected. The cupel correction can be disregarded.

Mr. F. C. Smith publishes an article in the *Trans. Am. Inst. Min. Eng.*, 26, 485, on "The Occurrence and Behavior of Tellurium in Gold Ores, etc.," which is partly devoted to the assay of telluride ores. His experiments prove that the crucible

assay is the better for telluride ores, and that the loss of gold in the assay is very great if the charge is not properly made up as regards the amount of litharge present. He does not locate the loss or make corrected assays.

In the discussion of Mr. Smith's paper, Mr. Wm. P. Jenney states that he believes an oxidizing charge with a small quantity of ore would be beneficial. The excess of litharge, of course, has an oxidizing action, but to try this point further the assays in Table IV were made by the following charge :

Ore, one-fifth assay ton.

Litharge, four assay ton.

Soda, one and a half assay tons.

Silica, one assay ton.

Six loops of wire.

Twenty grams of niter.

The wire acted as the reducing agent with the sulphur. The buttons were good and malleable, but on cupellation gave no better results than charges with litharge alone.

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## ON THE LINDO-GLADDING METHOD OF DETERMINING POTASH.

BY A. L. WINTON<sup>1</sup> AND H. J. WHEELER.<sup>2</sup>

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IN view of certain criticisms of the Lindo-Gladding method of potash determination which have appeared, of late, notably those by Vogel and Haefcke,<sup>3</sup> we were appointed a committee by the Association of Official Agricultural Chemists of the United States to prepare an article setting forth certain work bearing upon the points involved.

At the regular meeting of the Association in Washington in 1890, Frear and Sweetser<sup>4</sup> called attention to certain comparative determinations made by them, which indicated that the use of sodium chloride was unnecessary. The mean difference in

<sup>1</sup> Chemist Conn. Agricultural Experiment Station and Reporter on methods of potash determination for the Association of Official Agricultural Chemists for the years 1896 and 1897.

<sup>2</sup> Chemist R. I. Agricultural Experiment Station and Reporter on methods of potash determination for the Association of Official Agricultural Chemists for the years 1894 and 1895.

<sup>3</sup> Die landw. Versuch-Stationen 47 (1896), pp. 112-117.

<sup>4</sup> U. S. Dept. of Agr., Div. of Chem., Bull. 28 (1890), p. 73.

the results with and without sodium chloride amounted to but 0.04 per cent., and in but two cases out of fifty was the difference over 0.10 per cent. In 1891, Winton<sup>1</sup> investigated the matter thoroughly and in tests conducted with commercial potash salts and twenty-four mixed fertilizers, showed that the results with and without the addition of sodium chloride were practically identical.<sup>2</sup> The same line of study was further pursued in 1892 by Payne,<sup>3</sup> in cooperation with twenty-two chemists in seventeen different laboratories, working with a variety of substances. As a result of these investigations by the Association the use of sodium chloride was discontinued.<sup>4</sup> This was done not because inaccurate results were obtained by its use, but in order to abbreviate the method by striking out a cumbersome and useless detail.

Notwithstanding the fact that it had already been abundantly shown that there was practically no difference in the results obtained with and without the use of sodium chloride, Breyer and Schweitzer<sup>5</sup> asserted that its use was a source of error. Their claim that it was unnecessary was merely a reiteration of what had already been shown by the work of the Association.

Aside from the undesirability of employing sodium chloride the only unfavorable criticism of the Lindo-Gladding method worthy of note, which has appeared, is based upon the assumption that a considerable error is introduced through double decomposition resulting from contact of the ammonium chloride wash solution with potassium platinichloride. Breyer and Schweitzer<sup>6</sup> and N. Robinson<sup>7</sup> mention errors thus arising and the two former chemists claim that the amount of the same is considerable. Their conclusions in this respect are based chiefly upon the amount of potassium chloride said to have been recovered from the ammonium chloride wash solution which had already been employed in washing precipitates of potassium platinichloride. It does not appear, however, that blank determinations were made for the purpose of ascertaining the amount

<sup>1</sup> U. S. Dept. of Agr., Div. of Chem., Bull. 31 (1891), pp. 145-150.

<sup>2</sup> Compare Fresenius' *Ztschr. anal. chem.*, 16, 63.

<sup>3</sup> U. S. Dept. of Agr., Div. of Chem., Bull. 35 (1892), pp. 58-61.

<sup>4</sup> U. S. Dept. of Agr., Div. of Chem., Bull. 35 (1892), pp. 197, 198.

<sup>5</sup> *J. Anal. Appl. Chem.*, 6, (1892), 477.

<sup>6</sup> *J. Anal. Appl. Chem.*, 6, (1892), 474-477.

<sup>7</sup> This Journal, 16, (1894), pp. 366, 367.

of potash, if any, contained in the ammonium carbonate, ammonium oxalate, and in the seven grams of barium hydroxide and other reagents employed in the recovery of the potash. In view of the fact that considerable amounts of potash are frequently present in certain so-called chemically pure reagents employed in potash determinations,<sup>1</sup> it would appear that a large part of the potash, said by Breyer and Schweitzer to have been recovered from the wash solution, may have been derived from their reagents. It is obvious, therefore, that their results instead of serving as a proper basis for the criticism of a method, are themselves open to serious criticism.

The ammonium chloride wash solution experimented with by Breyer and Schweitzer was the same as that employed by the Association, the preparation of which is described in a succeeding foot-note. That a great amount of double decomposition may result with this solution, under exaggerated conditions, has been shown by the work of the Association<sup>2</sup> during 1894 and 1895. This fact alone furnishes no suitable basis for the condemnation of the method, provided the amount of error arising in the ordinary course of analysis is practically insignificant.

During the years 1894<sup>3</sup> and 1895<sup>4</sup> one of us (H. J. W.) conducted comparative determinations to learn whether washing with ammonium chloride solution, according to the Lindo-Gladding method, introduced an appreciable error. The analytical work was carried out with the cooperation of analysts of the Association of Official Agricultural Chemists of the United States, nine taking part during the first year and ten during the second year, no two of them working in the same laboratory or with the same reagents.

In 1894 portions of four grams each of pure potassium chloride were made up to one liter with water and twenty-five cc. of this solution, representing one-tenth gram of the salt, were taken for each determination. As the salt contained a small amount of water, which, in the portions sent to the different analysts, varied from 0.06 to 0.16 per cent., the results have in

<sup>1</sup> U. S. Dept. of Agr., Div. of Chem., Bull. 43 (1894), pp. 21, 22; also Bull. 47 (1895), pp. 16, 17; and Bull. 49 (1896), pp. 30-32.

<sup>2</sup> U. S. Dept. of Agr., Div. of Chem., Bull. 43 (1894), pp. 23, 24; and Bull. 47 (1895), p. 22.

<sup>3</sup> U. S. Dept. of Agr., Div. of Chem., Bull. 43, pp. 17-25.

<sup>4</sup> U. S. Dept. of Agr., Div. of Chem., Bull. 47, pp. 14-23.

each case been calculated to correspond with one-tenth gram of the dry material (see Table I).

TABLE I.

COMPARISON OF RESULTS ON PURE POTASSIUM CHLORIDE BY THE LINDO-GLADDING METHOD AND BY THE METHOD OF WASHING WITH ALCOHOL ONLY (1894). ONE-TENTH OF A GRAM OF POTASSIUM CHLORIDE TAKEN IN EACH DETERMINATION.

Analyst.	Potassium platinum-chloride washed with alcohol only. Potassium chloride found.	Potassium platinum-chloride washed with alcohol and ammonium chloride solution, (Lindogladling method). Potassium chloride found.	Results by washing with ammonium chloride are more (+) or less (-) than those without.
	Gram.	Gram.	Gram.
W. A. Powers, Illinois Station.....	0.10053	0.10134	
	0.10114	0.10159	
Average .....	0.10084	0.10147	+0.00063
F. P. Veitch, Maryland College ....	0.09867	0.09864	-0.00003
J. B. Lindsey, Massachusetts Station.	0.10112	0.10082	
	0.10066	0.10097	
	0.10066	0.10060	
		0.10005	
Average.....	0.10082	0.10061	-0.00021
W. L. Rossman, Michigan Station..	0.09957	0.09974	
	0.09951	0.09956	
	0.09957	0.09971	
	0.09933	0.09965	
Average .....	0.09950	0.09967	+0.00017
J. P. Street, New Jersey Station ....	0.09838	0.09807	
	0.09868	0.09838	
	0.09871		
Average .....	0.09859	0.09823	-0.00036
B. L. Hartwell, Rhode Island Station	0.09960	0.09898	
	0.09954	0.09913	
		0.09934	
Average .....	0.09957	0.09915	-0.00042
K. P. McElroy, U. S. Dept. of Agr .	0.10000	0.10015	
	0.10012	0.10040	
Average .....	0.10006	0.10028	+0.00022
R. de Roode, West Virginia Station.	0.09996	0.09993	-0.00003

The determinations carried out in 1895 were made on solu-



tions of fifty cc. each, containing from three-tenths to one gram of pure potassium chloride, thus exposing to the action of the ammonium chloride solution three to ten times as much potassium platinichloride as in the preceding year.

The salt used was from a new lot containing uniformly 0.45 per cent. of moisture; the weights of potassium chloride taken, as given in Table II, represent, however, the dry salt.

In the determinations of both years, each solution of the pure salt was evaporated to a paste with an excess of platinum solution. The residue, after cooling, was stirred for twenty minutes with thirty cc. of eighty per cent. alcohol (sp. gr. 0.8645) and the liquid decanted on a weighed Gooch crucible. The washing was further continued by decantation, using ten cc. portions of alcohol and stirring for from two to three minutes after each addition.

In some cases the salt, without further washing, was dried at 100° C. and weighed; in others it was first washed with six portions of ammonium chloride solution<sup>1</sup> of ten cc. each and finally with eighty per cent. alcohol, according to the Lindo-Gladding method.

Blank determinations were made by both methods on the reagents. From the analytical data secured in these determinations, which were given in full in *loc. cit.*, Tables I and II have been prepared.

In calculating the results the total weight of potassium platinichloride obtained in each determination was first corrected by deducting the average weight obtained by the same analyst from the reagents.

For the conversion of potassium platinichloride to potassium chloride the factor 0.3069<sup>2</sup> was employed for reasons stated later.

A careful study of the results given in the tables will make it evident that the potassium platinichloride was very slightly, if at all, acted upon by the ammonium chloride solution. Finkener<sup>3</sup> found that a saturated solution of ammonium chloride at 22° C., when in contact with finely divided potassium platinichloride

<sup>1</sup> A solution of 100 grams of ammonium chloride in 500 cc. of water, which had been shaken for from six to eight hours with five to ten grams of pulverized potassium platinichloride, allowed to settle over night, and filtered.

<sup>2</sup> Platinum 195.0, potassium 39.11, chlorine 35.45.

<sup>3</sup> Pogg. *Ann.*, 129, 627.

TABLE II.  
COMPARISON OF RESULTS ON PURE POTASSIUM CHLORIDE BY THE LINDO-GLADDING METHOD AND BY THE METHOD  
OF WASHING WITH ALCOHOL ONLY (1895).

Analyst.	Potassium platini chloride washed with alcohol only.			Potassium platini chloride washed with alcohol and ammonium chloride solution (Lindo-Gladding method).		
	Potassium chloride taken.	Potassium chloride found.	Potassium chloride error.	Potassium chloride taken.	Potassium chloride found.	Potassium chloride error.
	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.
W. A. Powers, Illinois Station .....				0.3976	0.3954	-0.0022
B. L. Hartwell, Rhode Island Station <sup>1</sup> .	0.4776	0.4780	+0.0004	0.3872	0.3871	-0.0001
	0.4458	0.4463	+0.0005			
	0.4665	0.4668	+0.0003	0.4534	0.4532	-0.0002
	0.5437	0.5442	+0.0005	0.4799	0.4797	-0.0002
G. Wm. Gray, West Virginia Station ..	0.5114	0.5110	-0.0004			
				0.5028	0.5002	-0.0026
				0.5080	0.5049	-0.0031
F. P. Veitch, Maryland College .....	0.5004	0.5002	-0.0002	0.5043	0.5058	+0.0015
	0.5666	0.5685	+0.0019	0.5149	0.5163	+0.0014
	0.5005	0.5027	+0.0022			
W. H. Allen, North Carolina Station ...			.	0.2987	0.2989	+0.0002
				0.2987	0.2988	+0.0001
				0.2987	0.2985	-0.0002

<sup>1</sup> These results have been corrected for an error in the original table.

TABLE II.—(Continued).  
COMPARISON OF RESULTS ON PURE POTASSIUM CHLORIDE BY THE LINDO-GLADDING METHOD AND BY THE METHOD  
OF WASHING WITH ALCOHOL ONLY (1895).

Analyst.	Potassium platinumchloride washed with alcohol only.			Potassium platinumchloride washed with alcohol and ammonium chloride solution (Lindo-Gladding method).		
	Potassium chloride taken.	Potassium chloride found.	Potassium chloride, error.	Potassium chloride taken.	Potassium chloride found.	Potassium chloride, error.
J. B. Lindsey, Massachusetts Station...	Gram. 0.4978	Gram. 0.4987 0.4986	Gram. +0.0009 +0.0008	Gram. 0.4978 0.4978	Gram. 0.4985 0.4979	Gram. +0.0007 +0.0001
W. G. Brown, U. S. Dept. of Agr. ....	0.6479 0.5731 0.4796	0.6506 0.5749 0.4798	+0.0027 +0.0018 +0.0002	0.5550 0.5557	0.5559 0.5560	+0.0009 +0.0003
J. P. Street, New Jersey Station .....	0.4978 0.4978	0.4981 0.4977	+0.0003 -0.0001	0.4978 0.4978 0.4978	0.4996 0.4993 0.4985	+0.0018 +0.0015 +0.0007
E. P. Stone, New Hampshire Station ..	0.5022 0.5883	0.5043 0.5902	+0.0021 +0.0019	0.5022 0.5883	0.5043 0.5902	+0.0021 +0.0019
A. L. Winton, Connecticut Station .....	0.5004 0.5331 0.5310	0.5013 0.5338 0.5313	+0.0009 +0.0007 +0.0003	0.5011	0.5010	-0.0001

chloride for one hour, decomposed but 0.27 per cent. of the latter. Since the Lindo-Gladding method, at least as applied to the potash salts, secures the double salt in a granular condition, which according to Finkener is not so rapidly acted on, and since operating with a Gooch crucible the ammonium chloride solution is not in contact with the double salt longer than two or three minutes, errors from this source would not be expected to be and, as numerous results show, are not appreciable. There are few if any analytical methods where the precipitate is absolutely insoluble in the wash liquid and it is absurd to discriminate against the Lindo-Gladding method for theoretical reasons which have no practical significance.

Breyer and Schweitzer state that it is very "doubtful whether the method of Lindo-Gladding is a simplification of Fresenius' method." At all events, it should be stated that the members of the Association after having given both methods an extended trial find the latter decidedly shorter.

Breyer and Schweitzer state that potassium platinichloride obtained by them by the Lindo-Gladding method contained impurities, notably magnesium and calcium sulphates, but as they give no figures it is to be assumed that the amounts present were not determinable.

If the potash exists as chloride, and chlorides of sodium, magnesium and calcium are the only soluble impurities, evaporation with platinum solution and washing with alcohol should yield pure potassium platinichloride, the salts of chloroplatinic acid with the other bases being readily soluble in alcohol. Were this not true neither the Lindo-Gladding nor the Stassfurt method would be practicable.

If, however, the bases mentioned are combined wholly or in part with sulphuric acid, the potassium platinichloride, obtained by the Lindo-Gladding method, is usually, after the first washing with alcohol, contaminated with magnesium and calcium sulphates, subsequent washing with ammonium chloride solution being depended upon to remove these impurities.

Magnesium sulphate is readily soluble in the ammonium chloride solution. Even when a very considerable amount is present, the first addition of the reagent removes almost instantly the greater part of it. Calcium sulphate does not dissolve so

readily but it is contained only in small amount in the potash manure salts on sale in the United States and the treatment with ammonium chloride solution effectually removes both this salt and the magnesium sulphate.

That this is true is shown by the figures obtained by one of us (A. L. W.) which are given in Table III. The results calculated from the weights of potassium platinichloride (together with many others equally accurate obtained by seven American chemists) were reported to the Association of Official Agricultural Chemists in 1896,<sup>1</sup> but those calculated from the weights of metallic platinum are here given for the first time.

The materials used were chemically pure potassium sulphate, which had been ignited until all water was removed, and three mixtures representing the water-soluble impurities contained in "sulphate of potash (ninety per cent.)," "sulphate of potash and magnesia," and "kainit." The solutions for analysis, representing half gram portions of the commercial potash salts named, were prepared by mixing weighed portions of the pure salt with the corresponding amounts of the mixtures of impurities, dissolved in each case in twenty-five cc. of water. The determinations of potash in these solutions presented the same analytical difficulties as would have been encountered in the analysis of the real commercial salts, but the exact amount of potash present was in each case known and the results obtained could be compared with theory.<sup>2</sup>

The Lindo-Gladding method of the Association<sup>3</sup> was strictly followed except in the case of kainit solution, which was evaporated directly with platinum solution, without previous separation of lime, as was originally directed by Gladding.<sup>4</sup> The potassium platinichloride was weighed on Gooch crucibles, reduced in hydrogen, washed with hot water, ignited, and finally

<sup>1</sup> U. S. Dept. of Agr., Div. of Chem., Bull. 49, pp. 27-38.

<sup>2</sup> At the present time only four Stassfurt products are used in any considerable amount for agricultural purposes in the United States; viz., "ninety per cent. sulphate of potash," or "high grade sulphate of potash," "sulphate of potash and magnesia," or "low grade sulphate of potash," "kainit," and "eighty per cent. muriate of potash." Each of these is reasonably uniform in composition, containing, in addition to the potash salts, a certain proportion of chlorides and sulphates of soda, magnesia, and lime. In making the mixtures above described, the average composition of the commercial salts, as published by the German Kali Works, was followed.

<sup>3</sup> U. S. Dept. of Agr., Div. of Chem., Bull. 46, p. 23.

<sup>4</sup> U. S. Dept. of Agr., Div. of Chem., Bull. 7, p. 41.

weighed as metallic platinum, all of which was accomplished without transfer.

The small amounts of potash in the "impurities" were determined by careful analysis and calculated as potassium sulphate.

The conversion factors employed were:  $K_2PtCl_6$  to  $K_2SO_4$ , 0.3587; and Pt to  $K_2SO_4$ , 0.8937. These were derived from the following atomic weights: Pt = 195.0, K = 39.11, Cl = 35.45, S = 32.06, O = 16.0.

The factors which have been commonly used in potash determinations (0.3056 for converting  $K_2PtCl_6$  to KCl, 0.3570 to  $K_2SO_4$ , and 0.19308 to  $K_2O$ ) are those based on an atomic weight of platinum long since abandoned. Fresenius<sup>1</sup> found in some determinations made on pure potassium chloride, shortly after the now accepted atomic weight of platinum was determined by Seubert<sup>2</sup> that the factor 0.3056 gave results nearer theory than the factor derived from the later atomic weights. But it has been shown by one of us (A. L. W.)<sup>3</sup> that when platinum solution is added to a concentrated solution of the potash salt, as was done by Fresenius, much of the potassium platinichloride separates out at once as a finely divided precipitate, which, examined under the microscope, may be seen to consist of radiating crystals, enclosing numerous globular cavities containing liquid. Part of the enclosed liquid is slowly driven off at 100°, more at 130°, and more still at 160° C. As Fresenius dried at 130°, the water was presumably only partially removed and for this reason the lower factor gave the best results.

Winton has further shown, however, that when the solution of the potash salt is so dilute that the addition of the platinum solution either forms no immediate precipitate or one that dissolves on heating, the potassium platinichloride deposits slowly, on evaporation, in the form of coarsely granular crystals which appear under the microscope to be almost entirely free from enclosed liquid and which dry as completely on heating three hours at 100°, as when heated for many hours at 130° and 160° C. When the salt is obtained by this latter method, as was the case in all the determinations of Tables I, II, and III, the factors

<sup>1</sup> *Ztschr. anal. Chem.*, 21, 238.

<sup>2</sup> *Ann. Chem. (Liebig)*, 207, 1.

<sup>3</sup> *This Journal*, 27, 453.

based on the latest atomic weights give satisfactory results. The fact that the results (given in Table III) obtained by the Lindo-Gladding method and calculated by the revised factor, agree closely with those calculated from the weight of the platinum and with theory, is of itself a strong indication of the purity of the potassium platinichloride and the perfection of the process. It is only in the case of methods which yield an impure double salt that it is necessary to resort to the unscientific procedure of retaining incorrect factors in order to compensate for errors of the method.

Vogel and Haefcke,<sup>1</sup> as their first point against the Lindo-Gladding method, claim that the addition of sodium chloride is unnecessary and is liable to prove a source of error. This intended criticism was made in 1896, five years after the matter was first considered by the Association and three years after the Association had ceased to employ it, a fact which they might have ascertained had they consulted the published records of the proceedings of the Association.

Again, Vogel and Haefcke, after calling attention to the well-known fact of the double decomposition which results when potassium platinichloride is acted upon by ammonium chloride, further add that proof is lacking to show that the ammonium chloride, even after having been brought in contact with potassium platinichloride, is not capable of effecting still further double decomposition. Assuming that such further action results to a degree which practically interferes with the accuracy of the method, they find therein another point against it. In fact two years before this theoretical criticism was published, the Association had shown that the wash solution was capable, under greatly exaggerated conditions of treatment, of further effecting a considerable amount of double decomposition; but at the same time, as has already been shown, it was proved that in actual analytical work the amount of error thus introduced was practically so small as to furnish no valid objection to the method. Vogel and Haefcke could have learned these facts also before their criticisms appeared, had they consulted the published records of the association whose official methods they were discussing. It must be conceded that upon theoretical

<sup>1</sup> Die landw. Versuchs-Stationen, 47, (1896), pp. 115-116.

TABLE III.  
RESULTS BY THE LINDO-GLADDING METHOD ON MIXTURES REPRESENTING "SULPHATE OF POTASH NINETY PER CENT.," "SULPHATE OF POTASH AND MAGNESIA," AND "KAINIT."

Taken impurities corresponding to 0.5 gram of	Potassium sulphate, pure salt, taken.	Potassium sulphate, in impurities, taken.	Potassium sulphate, total taken.	Potassium platinichloride found.	Platinum found.	Results calculated from weight potassium platinichloride.				Results calculated from weight platinum.	
						Potassium sulphate found.	Potassium sulphate error.	Gram.	Gram.	Potassium sulphate found.	Potassium sulphate error.
"Sulphate of potash 90 per cent." .....	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.
	0.4042	0.0002	0.4044	1.1248	0.4523	0.4035	-0.0009	0.4042	-0.0002	0.4042	-0.0002
	0.4121	0.0002	0.4123	1.1483	0.4615	0.4119	-0.0004	0.4124	+0.0001	0.4124	+0.0001
"Sulphate of potash and magnesia" .....	0.4110	0.0002	0.4112	1.1448	0.4591	0.4106	-0.0006	0.4103	-0.0009	0.4103	-0.0009
	0.3040	0.0003	0.3043	0.8470	0.3408	0.3038	-0.0005	0.3046	+0.0003	0.3046	+0.0003
	0.2686	0.0003	0.2689	0.7490	0.3017	0.2687	-0.0002	0.2696	+0.0007	0.2696	+0.0007
"Kainit" .....	0.2566	0.0003	0.2569	0.7136	0.2866	0.2560	-0.0009	0.2561	-0.0008	0.2561	-0.0008
	0.1387	0.0005	0.1392	0.3860	0.1547	0.1385	-0.0007	0.1383	-0.0009	0.1383	-0.0009
	0.1727	0.0005	0.1732	0.4807	0.1922	0.1724	-0.0008	0.1718	-0.0014	0.1718	-0.0014



grounds only, many valuable and reliable methods of analysis would have to be discarded if the solvent action of the wash liquids, regardless of the degree of solubility, were the sole basis for such a procedure.

The variation in the time employed in washing the potassium platinichloride due to unequal rapidity of filtration and the size of the crystals to be washed, are also urged by Vogel and Haefcke as logical objections to the method. However, by the use of the Gooch crucible and by precipitating the potassium platinichloride from dilute solutions by which large crystals are obtained, it must be obvious and in fact it has been shown by abundant analytical data, that these objections hold only from a theoretical, and not from a practical, standpoint.

Vogel and Haefcke still further assert, based upon assumption or upon the previously mentioned statements of Breyer and Schweitzer, that the potassium platinichloride obtained by the Lindo-Gladding method contains many impurities and therefore that it is not advisable to weigh the double salt as such. However, as has been shown by the results in Table III, the potassium platinichloride obtained by the Lindo-Gladding method even in the presence of such impurities as are in commercial ninety per cent. sulphate of potash and sulphate of potash and magnesia, as well as in kainit, is practically pure and the results accord as closely as could be desired with those obtained by reduction and weighing the metallic platinum.

From what has been said above it will be seen that Vogel and Haefcke were not well informed as to the work of the Association nor in relation to the status of the method in vogue when their unfavorable criticisms were made; furthermore, they present no analytical data of their own in support of their assumptions and in the main the points which they sought to make were but a reiteration of the previous unfavorable criticisms of Breyer and Schweitzer, which have been shown by abundant data to have been, so far as practical considerations go, utterly unfounded.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF LAFAYETTE  
COLLEGE.]

## A NEW VOLUMETRIC METHOD FOR THE DETERMINA- TION OF COPPER.

BY RICHARD K. MEADE.

Received May 2, 1898.

THE average analyst is often deterred from the use of a volumetric method by the necessity of making and standardizing a special solution. In many cases it takes nearly as much time to ascertain the strength of the required solution as it does to make the analysis itself, and the standardization and analysis together render the volumetric method frequently as slow, if not slower, and vastly more troublesome than the gravimetric determination.

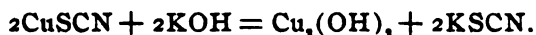
Volumetric analysis, therefore, becomes more and more an ideal method of quantitative determination as it approaches the requirement of a single standard solution, capable of having its strength accurately determined by simple means, giving a single, definite, clear end-reaction.

In iron and steel laboratories permanganate is fast coming to the front as a help to rapid analysis. Iron, phosphorus, manganese, sulphur (Payne's iodine solution is prepared by adding standard permanganate to potassium iodide) and calcium can all be quickly determined by the use of one standard solution. While it may never be possible to supplant other standard solutions by permanganate, still the sphere of its usefulness is a large one and is constantly enlarging.

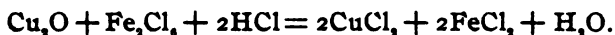
For a year or more I have been experimenting upon a new method for the determination of copper by permanganate, which seems to possess many points of superiority over the old one of reduction by grape sugar. In general it is as follows: The copper is brought into solution as a sulphate, either by dissolving it in sulphuric acid or evaporation of its solution with sulphuric acid. The greater part of the free acid is neutralized by ammonia, the solution warmed, sulphurous acid added until the solution smells strongly of the reagent, and then a slight excess of ammonium or potassium thiocyanate.<sup>1</sup> The copper

<sup>1</sup> Rivot: *Compt. rend.*, 38, 868; and Busse: *Ztschr. anal. Chem.* 1878, 55.

is immediately precipitated as cuprous thiocyanate. Stirring and warming renders the precipitate heavy and easily handled. The solution is filtered through asbestos, using the pump, and well washed. The precipitate and filter are thrown into the beaker in which the precipitation was made and heated with a solution of caustic soda or caustic potash. Double substitution takes place. Hydrated cuprous oxide and potassium or sodium thiocyanate result.



The oxide is filtered on asbestos and washed well with hot water. The precipitate and filter are again placed in the same beaker and an excess of ferric chloride or ferric sulphate (free from nitric acid, free chlorine or ferrous salts) together with a little dilute sulphuric acid added. The copper oxide reduces a corresponding amount of iron from the ferric to the ferrous condition.



The beaker is warmed and stirred until all the copper oxide is dissolved. The solution is then poured through a perforated platinum disk and the asbestos which stays behind upon it washed with water, to which has been added a little sulphuric acid and a little ferric chloride or sulphate. The solution is then titrated with permanganate. The iron equivalent to the permanganate used multiplied by 1.125 gives the weight of copper in the sample.

Instead of sulphurous acid, ammonium or sodium bisulphite may be used to reduce the copper. A solution of equal weights of sodium bisulphite and potassium thiocyanate answers well as a reagent for the precipitation of the metal. Since copper is the only metal precipitated by an alkaline thiocyanate from an acid solution, the presence of arsenic, antimony, bismuth, zinc, and other materials which render the electrolytic, the cyanide, and the iodine method inaccurate, will not affect the results.

The caustic alkali solution, used to convert the cuprous thiocyanate into cuprous hydroxide, must not be too strong or some of the metal will go into solution, coloring the liquid blue. I have used about a half normal solution of caustic potash,

made by dissolving twenty-eight grams of the salt in a liter of water. Either ferric sulphate or ferric chloride may be used to dissolve the cuprous oxide. The former is probably the safest, but the latter appears to dissolve the precipitate the more readily of the two.

As a test of the accuracy of the method four grams of pure electrolytic copper were dissolved in nitric acid and the solution evaporated with sulphuric acid until the nitric acid was expelled. The solution was cooled and diluted to one liter. The copper contained in fifty cc. was then determined electrolytically with the following result:

	Gram.
1.....	0.2003
2.....	0.2003
3 .....	0.2000
4.....	0.1997
<hr/>	
Average .....	0.2001

The copper in fifty cc. was next determined by the thiocyanate-permanganate method outlined above. The permanganate solution used was made by dissolving 5.02 grams of pure crystallized potassium permanganate in water and diluting after standing twenty-four hours to two liters. Its strength was determined by titration against iron wire and against ferrous ammonium sulphate.

Against ferrous ammonium sulphate :

	Gram iron.
1. One cc. =	0.004455
2. One cc. =	0.004456

Against iron wire :

	Gram iron.
3. One cc. =	0.004460
4. One cc. =	0.004449

Average one cc. = 0.004455

One cc. = 0.004455  $\times$  1.125 = 0.005012 gram copper.

Below are the results on fifty cc. of the copper solution containing 0.2001 gram copper by the thiocyanate-permanganate method :

No.	Permanganate. cc.	Copper. Gram.
1 .....	39.6	0.1985
2 .....	39.5	0.1980
3 .....	39.6	0.1985
4 .....	39.7	0.1990
5 .....	40.0	0.2004
6 .....	39.8	0.1995

In determinations numbers 1, 5, and 6, ferric chloride was used to dissolve the cuprous oxide; in numbers 2, 3, and 4, ferric sulphate was used.

As a further and more practical test of the method, the copper in some samples of copper ore was carefully determined by the electrolytic, and then by the thiocyanate-permanganate method. Below are the comparative results :

Sample.	Weight of sample. Gram.	Perman- ganate. cc.	Copper by thiocyanate- permanganate method. Per cent.	Copper by electrolytic method. Per cent.
1. Chalcopyrite I.....	1.0	39.6	19.85	19.95
2. " .....	1.0	39.3	19.70	19.86
3. Chalcopyrite II.....	2.0	24.6	6.16	6.37
4. " .....	2.0	24.8	6.21	6.30
5. Malachite .....	1.0	72.2	36.19	36.10
6. " .....	1.0	72.2	36.19	36.15
7. Tetrahedrite.....	1.0	42.0	21.05	21.06
8. " ... ..	1.0	41.7	20.90	21.18

It will be seen by the above results that the method is accurate enough for ordinary commercial purposes. In spite of its three filtrations, the method is quite rapid. Not counting the time required for the solution of the ore, duplicate analyses can be easily made in from a half to three-quarters of an hour.

In the writer's opinion the process is superior to both the iodine and the cyanide method. It requires the use of no rapidly changing solutions, but one which every analyst has on hand nearly all the time. The end-reaction is clear, distinct, and familiar to all chemists. The method is applicable to any ore, matte or alloys. It is as rapid as the cyanide, except in certain cases favorable to the latter, and more rapid than the iodine method. Finally, not the least of its points of advantage is that it is more accurate than either of the two.

# ON THE SEGREGATION OF CARBON IN A PIECE OF BOILER PLATE.

BY HENRY FAY AND HENRY P. TALBOT.

Received June 15, 1898.

A PIECE of steel has recently come into our hands for examination which, by its unusual and striking properties, strongly emphasizes the necessity for careful heat treatment. The specimen was a circular steel plate, one-fourth inch in thickness and about three feet in diameter, and was intended for use as the head-piece of a pressure cylinder to hold carbon dioxide.

Unfortunately, the complete history of the piece was not obtainable, but it is known that after its receipt from the manufacturers the plate was twice annealed and was then to be punched into a cup-shaped cylinder head. On flanging, however, the plate cracked around the entire bend, which was made about four inches from the circumference, the cracks being fully one-sixteenth inch deep and more than an inch long.

Samples for analysis were taken from the edge of the plate and from the center, and test pieces were also taken from both portions for examination as to tensile strength and elongation. The specifications called for a mild steel containing about 0.30 per cent. carbon.

The results of the analysis are tabulated below :

	Outer portion. Per cent.	Center portion. Per cent.
Phosphorus.....	0.005	0.006
	0.004	0.008
	0.003	0.005
	0.006	0.005
	....	0.004
Sulphur .....	0.033	0.050
	0.042	0.050
	0.033	0.040
Manganese .....	0.36	0.38
	0.37	0.38
Carbon .....	0.130	0.087
	0.036	0.070
	0.110	0.124
	0.156	0.060
	0.067	0.090
	0.080	0.030
	0.076	0.091
	....	0.070
	....	0.100

It will be noted that, with the exception of the carbon and sulphur, the percentages represent about normal values for a steel which would be suitable for the purpose named.

The carbon determinations, on the other hand, exhibit the most astonishing variations, ranging between 0.036 and 0.156 per cent. in the outer portions, and 0.060 and 0.124 per cent. in the center. A thorough examination of chemicals and apparatus, and repeated blank analyses, made it certain that errors from these sources were eliminated, and it only remained to conclude that the varying percentages represented inequalities in the composition of the material under analysis.

For the physical tests, made by Professor E. F. Miller, of the Massachusetts Institute of Technology, three test pieces were taken, one of which was from the flange where the crack showed, the others from the unbent portion. The specimen from the flange was straightened by being heated to a bright cherry-red, and the tensile strength was determined in the usual way. The fracture did not take place at the point where the crack occurred, as one might expect.

The following results were obtained :

	1.	2.	3. Test-piece from flange.
Dimensions of cross-section...	2" X 0.3850"	2" X 0.3850"	2" X 0.380"
Tensile strength.....	44,690	44,670	45,960
Elongation.....	28.1	....	....

It will be seen that the material would probably have been rejected on account of low tensile strength, not to mention the fact that the carbon determinations had shown the material to be far from homogeneous.

The results of the physical tests, however, threw no light upon the cause of the inequalities in the carbon contents of the steel, but upon etching a small, roughly polished portion with dilute nitric acid (sp. gr. 1.13), the fact was at once demonstrated that the steel was badly crystallized.

Other portions of the plate were then cut and carefully polished with various grades of emery and finally with rouge. This polishing served to etch the samples sufficiently to permit of an examination with the microscope which, in turn, showed the carbon to be unevenly distributed throughout the mass.

Upon etching the surface a trifle more deeply, in relief, with dilute nitric acid (sp. gr. 1.13), the grains of ferrite were very clearly brought out, as can be seen in the accompanying cut (Fig. 1), which represents the crystals in their natural size.

A similar examination of the edge of the plate made it evident that the crystallization had penetrated only part way through the mass. A glance at Fig. 2 will show the depth to which the crystallization had extended.

The test pieces which were subjected to the tensile tests also show this superficial crystalline structure in a peculiar way. Instead of pulling uniformly and breaking sharply, the crystalline layers slipped along on the non-crystalline portion and the surface was more or less pitted as a result of the depression of some of the crystals and the elevation of others, caused by the breaking apart of the separate crystals. The uniformity with which the crystalline structure has penetrated the metal, and this slipping of the two layers would seem to suggest that the plate was the "composition metal" of trade, or had been made by the process of "piling." Without a knowledge of the early history of the plate it is impossible to speak conclusively upon this point.

Sauveur<sup>1</sup> has shown experimentally that (a) "a slow and undisturbed cooling from a temperature  $x$  or higher, produces crystallization; (b) undisturbed cooling from an initial temperature lower than  $x$  is not accompanied by crystallization; (c) the higher the initial temperature from which the steel is allowed to cool undisturbed, the larger the grain for a given composition." Again, Osmond,<sup>2</sup> in discussing the heat treatment of steels, states that "in proportion as the temperature of annealing is elevated, the polyhedra of ferrite increases in size."

In the specimen under examination the grains of ferrite are not only visible to the unaided eye but some of them are of unusual size, measuring in transverse section as much as  $1.5 \times 1$  cm., and there is further evidence of the faulty heat treatment in the microstructure which shows an uneven distribution of the pearlyte. There is therefore very little doubt that this specimen of steel has been subjected, during the annealing process, to a

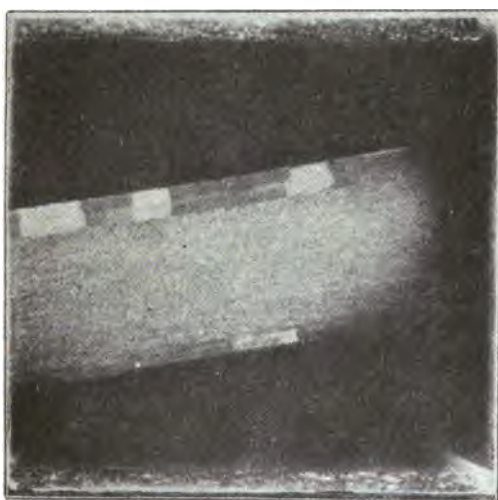
<sup>1</sup> *Trans. Am. Inst. Min. Eng.*, 22, 546.

<sup>2</sup> *Ibid.*, 22, 255.





**Fig. 1. Showing grains of Ferrite. Natural size.**



**Fig. 2. Side view. Showing depth of crystallization.**



**Fig. 3. Magnified about 30 diameters.**



temperature materially higher than that required, and has been allowed to cool extremely slowly. It is more than probable that the crystallization took place during the annealing process rather than during the manufacture of the plate, for the reason that cooling of the plate after rolling would necessarily be more rapid than after annealing, and to produce crystals of such size would require slow and undisturbed cooling.

The fact that the steel was overheated was further attested by the unusual thickness of the scale.

With respect to the variations in the percentage of carbon, it is safe to assume that the high temperature burned out a portion of the carbon and what remained had segregated during the process of crystallization, particles of carbon being distinctly visible on the polished surface with the help of a hand magnifying glass. That such a segregation of carbon may take place during crystallization is well demonstrated in a piece of open-hearth steel (kindly sent to us by Mr. Kreuzpointer of the Pennsylvania Railroad Laboratory of Tests), which had broken through the bottom of the furnace and over which more than three hundred heats had been made. That the polished and etched surface shows a marked similarity to that of the steel for the pressure cylinder is evident from Fig. 3, which shows well-marked crystals of ferrite, and the portion standing in relief is the segregated carbon, which can be seen in the sample with the unaided eye.

As has already been stated, the sharp line of demarcation between the crystalline exterior and non-crystalline interior, as shown in Fig. 2, suggests a "composition metal" and there is no definite evidence to disprove this. It may not, however, be out of place to ask the question: whether, if the heating of the plate in the furnace, although too strong, had yet been sufficient to effect it but partially, and if it had been at once transferred to the annealing oven where it could cool slowly, a similar result with respect to crystallization might not be within the bounds of possibility. Whether then the finished piece was originally composition metal or had been produced by the heating alone, there can be no doubt that it was ruined by the heat treatment.

## THE MINERAL CONSTITUENTS OF THE TUBERCLE BACILLI.

BY E. A. DE SCHWEINITZ AND MARION DORSET.

Received April 14, 1898.

IN August, 1895,<sup>1</sup> the writers published the results of some analyses showing the composition of the tubercle bacilli when grown upon different media. Depending upon the character of the media used, the amount of ash varied from two to four per cent. It seemed desirable to make a careful analysis of the ash in order to see which of the mineral constituents of the animal body would be most largely utilized by the germ and consequently necessary for its satisfactory development. The bacilli used for this work had been grown upon neutral beef broth containing one per cent. of peptone, one-half per cent. salt, and seven per cent. glycerol. The cultures, after heating in order to kill the germs, were filtered and washed well with boiling water. The washed bacilli were then dried over sulphuric acid, finely powdered, and thoroughly extracted with pure ether and ninety-eight per cent. alcohol. After the last extraction the bacilli were again dried and ignited at a low red heat until practically all the carbon had been burned. The ash, which was almost pure white in color, was dried to a constant weight at 100° C. The total ash available for analysis was 1.453 grams. Examination showed that sulphates, chlorides, and carbonates were not present in the ash. The method used for the determination of the constituents of the ash were those prescribed for the analyses of the ash of plants. The results calculated upon the dry ash were as follows :

	Per cent.
Na <sub>2</sub> O .....	13.62
K <sub>2</sub> O .....	6.35
CaO .....	12.64
MgO .....	11.55
C and Si .....	0.57
P <sub>2</sub> O <sub>5</sub> .....	55.23

The high percentage of phosphorus pentoxide and the absence of other acid radicals in this ash are very noticeable. While it is probable that some of the chlorides and sulphates

<sup>1</sup> This Journal, 17, 605.

may have been washed out of the germ in the process of preparing it for analysis, no chlorides were present in the germs after washing; the fact that the amount of phosphoric acid obtained in the ash is slightly lower than the total amount of phosphoric acid obtained from the whole germ, would indicate that chlorides and sulphates are practically of no importance in the composition of the germ, while their presence in the culture media in minute quantity appears to be necessary for the satisfactory development of the germ. Chlorides and sulphates if dissolved out would have been present probably as cell contents rather than as part of the germ.

Ash analyses of comparatively few germs have been made, and the only ones which give data that may be reported here are the analyses made by Cramer,<sup>1</sup> who found that the composition of the ash of the cholera germs varied greatly, depending upon the quantity of sodium chloride and sodium phosphate that were used in the preparation of the media. In normal media the results were as follows:

	Per cent.
Cl.....	17.02
P <sub>2</sub> O <sub>5</sub> .....	20.48
SO <sub>4</sub> .....	8.55
K.....	6.32
Na.....	32.06
Ca.....	0.98
Mg.....	trace

If the amount of sodium chloride in the media was increased, the percentage of chlorine in the ash was more than doubled, while the percentage of SO<sub>4</sub> found was reduced to one per cent., and the percentage of P<sub>2</sub>O<sub>5</sub> was largely diminished, being reduced to 9.64 per cent. When sodium phosphate was added to the media the percentage of chlorine was found to be 9.99 per cent., the percentage of P<sub>2</sub>O<sub>5</sub> 34.30 per cent., SO<sub>4</sub> 2.24 per cent., of potassium 4.97 per cent., of sodium 31.83 per cent., of calcium 1.29 per cent., of magnesium 0.12 per cent. These results differ greatly from those found in the examination of the ash of the tubercle bacilli. As noted above, the media used for the growth of these latter germs was a normal material containing one-half per cent. of salt, but without the addition of any

<sup>1</sup> *Archiv. für Hygiene*, 28, No. 1.

phosphates or other salts. Consequently the high percentage of phosphorus pentoxide can be attributed only to the fact that phosphorus as well as the calcium and magnesium are absolutely necessary for the development of the tubercle bacilli, and were derived by it from these elements as normally present in the media.

In arrested cases of tuberculosis in animals, we often find hard, gritty, calcareous nodules. These nodules in healed tuberculosis contain tubercle bacilli. In other cases of healed tuberculosis where calcareous nodules are not present no bacilli as a rule are found. It is easy to trace a very close connection between these nodules in healed tuberculosis, and the composition of the ash of the germ.

The high percentage of fat contained in the body of the tubercle bacilli, which we have noticed in previous papers, in conjunction with this high percentage of calcium and magnesium phosphate in the ash, give grounds for some interesting speculation. Phosphates and cod-liver oil are two materials always strongly recommended in cases of tuberculosis. As the germs of this disease seem to demand a large quantity of food containing phosphorus and also rich in fat, it is but a fair supposition that in giving the drugs above mentioned, we are supplying to the animal body those constituents which are very important for its proper nourishment, the supply of which is constantly being levied upon by the germs of the disease. The question might be asked whether in this method of treatment we are not really feeding the bacilli rather than the individual. But just as an exhausted soil can be made valuable by the addition of constituents which are deficient, so we may assume that the administration of specific materials containing the elements that the germ has utilized, should act in a similar way in increasing the vitality in the animal body. These of course are speculations, based, however, on certain known data. We trust that a still further study which is in progress, including the albuminoid constituents of the tubercle bacilli, may throw some light upon their development and chemical action in the animal body.

## THE SPECIFIC GRAVITY OF SODIUM CHLORIDE SOLUTIONS.

By H. C. HAHN.

Received April 8, 1898.

THE specific gravity and expansion by heat of salt solutions have not received the attention of chemists and physicists to the extent which they deserve. The data for common salt, for example, are only sufficient for technical purposes.

To the best known determinations of the specific gravity of sodium chloride solutions belong those of J. A. Bischof, G. Karsten, and G. T. Gerlach. Since the publication by Bischof in 1810, so many improvements in physical apparatus and more exact determinations of certain necessary factors, have been made, that we need not take his determinations into consideration. Those of G. Karsten, in 1846, show extraordinary diligence. His method is to weigh a glass ball in a salt solution, which stands in a large vessel full of water to be heated gradually. In this method there is danger of the one beam of the balance getting warmer than the other by the ascending current of heated air from the lamp and the hot water. Nevertheless, his method is the best, if modified as explained below. Further, Karsten did not determine the coefficient of expansion of his glass ball, but used the one determined by Munke, which is not admissible in very exact determinations. He does not state that the degrees of the mercurial thermometer were corrected to those of the air thermometer; nor that in calculating the weight of the weights and the glass ball in the vacuum, he took into consideration the amount of water and carbon dioxide in the air. The determinations by Gerlach<sup>1</sup> are the best; but some of the same and some other objections have to be raised against them. He did not determine the coefficient of expansion of his pycnometer, but used the one of Dulong and Petit. Reducing the weights to the vacuum, he assumed the atmosphere to have been saturated with water, which very probably was not the case. He compared the different specific gravities with that of water of 15°, instead of with that of 4°. He did not correct the degrees of the mercurial thermometer, and

<sup>1</sup> Spec. Gewichte der gebräuchlichsten Salzlösungen von verschiedenen Concentrationsgraden, Freiberg, 1859.

instead of calculating a formula for each series of determinations, he calculated the specific gravities of the solutions of certain percentages by interpolation from the two nearest determinations. Some of these defects may yet be corrected. This I have done and give in the following the details with different methods to eliminate errors.

Sodium chloride. Per cent.	Sp. gr. at 15° of mercurial thermometer compared with water of 15°.	Sp. gr. at 15.08° of air thermometer compared with water of 4°.
	1.	2.
0	1.000 00	0.999 12
5	1.036 24	1.035 33
10	1.073 35	1.072 40
15	1.111 46	1.110 48
20	1.151 07	1.150 05
25	1.192 28	1.191 23
Saturated at 15°	1.204 33	1.203 27

For the numbers in column 1 different formulas may be calculated, according to the number of figures used. To the values for five, ten, twenty, and twenty-five per cent. corresponds the formula :

$$s = 0.999,03 + 0.007,203p + 0.000,009,4p^2 + 0.000,000,4p^3,$$

when  $s$  signifies the specific gravity and  $p$  the per cent. of sodium chloride. But the values for naught and fifteen per cent., as calculated by this formula, would be : 0.999,03 and 1.110,54, which are slightly erroneous.

A formula calculated according to the method of least squares, with the use of the 4th power is :

$$s = 0.999,12 + 0.007,072,54p + 0.000,024,206,76p^2,$$

which gives the values of column 3. The sum of least squares is 0.000,000,175.

3.	4.
0.999,12	0.999,12
1.035,09	1.035,12
1.072,26	1.072,30
1.110,65	1.110,69
1.150,25	1.150,27
1.191,06	1.191,04

The differences of the observed and calculated values are larger than of those obtained by the foregoing formula. I calculated



therefore another one with the use of the 5th and 6th power:

$$s = 0.999,12 + 0.007,079,96p + 0.000,023,844,27p^2 + 0.000,000,001,002,876p^3,$$

which gives the numbers in column 4, with the sum of least squares = 0.000,000,177,6, which is no improvement on the former formula.

As a specimen of such calculations, I give here the items for the last formula :

8.				
$0.999,12 = a$				
$1.035,33 = a + 5x + 5^2y + 5^3z$				
$1.072,40 = a + 10x + 10^2y + 10^3z$				
$1.110,48 = a + 15x + 15^2y + 15^3z$				
$1.150,05 = a + 20x + 20^2y + 20^3z$				
$1.191,23 = a + 25x + 25^2y + 25^3z$				
$p^2.$	$p^3.$	$p^4.$	$p^5.$	$p^6.$
25	125	625	3,125	15,625
100	1,000	10,000	100,000	1,100,000
225	3,375	50,625	759,375	11,390,625
400	8,000	160,000	3,200,000	64,000,000
625	15,625	390,625	9,765,625	244,140,625
1375	28,125	611,975	13,828,125	320,546,875
$p(s-a).$	$p^2(s-a).$	$p^3(s-a).$	$p^4(s-a).$	$p^5(s-a).$
0.181,05	0.905,25	4.526,25	73.280,00	375.840,00
0.732,80	7.328,00	60.372,00	120.068,70	3,001.718,00
1.670,40	25.056,00	213.729,95	4,622.804,25	
3.018,60	60.372,00			
4.802,75	120.068,70			
10.405,60	213.729,95			

According to the method of least squares, we have the following equations :

$$\begin{aligned} p(s-a) &= p^2x + p^3y + p^4z \\ p^2(s-a) &= p^3x + p^4y + p^5z \\ p^3(s-a) &= p^4x + p^5y + p^6z \end{aligned}$$

Substituting into these equations the values obtained above, they become :

$$\begin{aligned} 10.405,60 &= 1,375x + 28,125y + 611,975z \\ 213.729,95 &= 28,125x + 611,975y + 13,828,125z \\ 4,622.804,25 &= 611,975x + 13,828,125y + 320,546,875z \end{aligned}$$

which further developed give the last formula mentioned above.

Another method is to calculate series of differences of the numbers of the main series. The method is only applicable if the values of  $p$  rise or fall in an arithmetical proportion.

The series 2 above gives the following series of differences :

0.999,12				
1.035,33	3621			
1.072,40	3707	86		
1.110,48	3808	105	15	Average. 25
1.150,05	3957	149	48	
1.191,23	4118	161	12	

Since each arithmetical series of the  $n$ th degree gives  $n$ , and only  $n$  series of differences, we know at once to which degree the desired formula belongs.

In reconstructing the main series and the series of differences backward, from the first member of the series, *i. e.*, 3621, 86, 25, we get the values given below in column 5.

If  $s$  is the first member of the main series,  $ds$  that of the first difference series,  $d_s s$  that of the second, etc., the  $n$ th member of the main series is :

$$S_n = s + (n-1) ds + \frac{(n-1)(n-2)}{1 \times 2} d_s s + \frac{(n-1)(n-2)(n-3)}{1 \times 2 \times 3} d_s s.$$

The sixth member of the main series is therefore :

$$S_6 = s + 5ds + \frac{5 \times 4}{1 \times 2} d_s s + \frac{5 \times 4 \times 3}{1 \times 2 \times 3} d_s s.$$

If we substitute in this equation for  $ds$  the value 3620, the second member of the main series will be found to be too small by 1; the third by 2; the fourth by 3. If for  $d_s s$  we substitute 85, the third member will be too small by 1; the fourth by 3; the fifth by 6, and the sixth by 10. A similar result is obtained if for  $d_s s$  we substitute 24. By diminishing  $ds (= 3621)$  by 1, we get numbers which correspond best with those observed, with the sum of least squares equal to 0.000,000,000,54. They are given in column 6.

5.	6.			
0.999,12	0.999,12			
1.035,33	1.035,32	3620		
1.072,40	1.072,38	3706	86	
1.110,58	1.110,55	3817	111	25
1.150,12	1.150,08	3953	136	25
1.191,27	1.191,22	4114	161	25

To calculate a formula for the values of column 6, we have the following points to consider. The first member of the formula will be: 0.999,12, and the fourth equal to  $\frac{0.00025}{1 \times 2 \times 3 \times 5}$ ,  $= 0.000,000,333,333$ . Any two values of the main series will give the second and third members of the formula, thus:

$$s = 0.999,12 + 0.007,1707 p + 0.000,0122 p^2 + 0.000,000,333,333 p^3.$$

It is generally believed that by the method of least squares formulas corresponding best with the observed values are obtained; but we see that the method of series of differences may give a better result. The above tables and formulas are not convenient in practice, in which generally the specific gravity is known and the per cent. of sodium chloride is sought. It is therefore necessary to construct another formula, corresponding to the reversed condition, for which purpose any four values of column 6 should be sufficient. But it was found impossible to construct out of four, or all six of the numbers, a formula of the third degree which would give exactly the values of column 6.

I calculated therefore from the last formula the per cent. of sodium chloride in a solution whose specific gravity is a little less than 1.00, and likewise the per cent. of sodium chloride in a solution whose specific gravity is a little more than 1.00; and similarly for the solutions of 1.05, 1.10, 1.15, 1.20, 1.25 specific gravities, and found by interpolation the per cent. corresponding to the desired specific gravity. For example:

	Specific gravity.
0.1 sodium chloride	= 0.999,84
0.2 " "	= 1.000,55
Difference 0.1 " "	= 0.000,71

Therefore 0.077,46 per cent. sodium chloride = 0.000,55 specific gravity.

$0.2 - 0.077,46 = 0.122,54$  per cent. sodium chloride solution has the specific gravity of 1.00.

In this way the values of column 7 were obtained.

Specific gravity.	7. Per cent. sodium chloride.					
1.00 =	0.122,54					
1.05 =	6.995,95	6.873,41				
1.10 =	13.633,77	6.637,82	0.235,59			
1.15 =	19.990,12	6.356,35	0.281,47	0.045,88		
1.20 =	26.040,00	6.049,88	0.306,46	0.025,00	0.020,88	
1.25 =	31.777,53	5.737,73	0.312,35	0.005,88	0.019,12	

It is seen at once that with a trifling change a formula of the fourth degree can be calculated, whose second and fourth members are preceded by a minus sign, because the first and third series of differences are diminishing from top to bottom, and

whose fifth member is:  $\frac{0.02 \times 20^4}{1 \times 2 \times 3 \times 4} = 133,333,333.$

A minimum of changes is obtained if the third series of differences is made the following: 0.045,44, 0.025,44, 0.005,44, and hence we get the following main series:

8.					
0.122,485					
6.996,005	6.873,52				
13.633,715	6.637,71	0.235,81			
19.990,175	6.356,49	0.281,25	0.045,44		
26.039,945	6.049,77	0.306,69	0.025,44	0.02	
31.777,585	5.737,64	0.312,13	0.005,44	0.02	

from which the following formula is calculated:

$$\text{Per cent.} = 60.209,585 - 626.853,15 + 1067.352,667s^2 - 633.92s^3 + 133,333,333s^4,$$

which, if the specific gravity at  $15.08^\circ$  air thermometer is known exact to the fourth decimal, will give the per cent. of sodium chloride exact to 0.01.

Gerlach determined also the expansion by heat of different solutions of sodium chloride. I tried to find a formula for his values according to the method of least squares, with the help of the fifth power of the temperature; but the calculated values showed differences in the average of 0.000,33 (the largest was 0.000,62).

A main factor in determinations of specific gravity is the knowledge of the specific gravity of the air in the balance case, which depends on the barometric pressure, temperature, and its percentage of water and carbon dioxide. More exact than by calculation is the direct determination, which is made in the same manner as the determination of the specific gravity of the liquid itself. For this purpose I recommend the use of three solid gilded cylinders of pure aluminum of precisely the same weight. Cylinders are to be preferred to globes, and a metal is to be preferred to glass, because cylinders and metal acquire more quickly the temperature of the surrounding medium, and are more conveniently made of equal volume. Each cylinder should weigh at least twenty grams. Since the specific gravity of aluminum is 2.67, a cylinder of two cm. diameter and three cm. length weighs 25.16 grams in air, 9.42 grams in cold water, and 7.95 grams in a liquid of 1.25 specific gravity.

A balance, which indicates one-tenth milligram under a load of 25 grams, will indicate only about five-tenths to one milligram, if the cylinder to be weighed is immersed into a very heavy liquid, so that the weight, respectively loss of weight of a twenty-five gram cylinder in a liquid of 1.25 specific gravity, may be ascertained within the  $\frac{0.001}{25} = 0.00004$  part of 1; therefore the specific gravity is correct within at least the fourth decimal.

Before gilding, a hook of platinum wire is fastened to the end of each cylinder. The exact equal weight being established, the cylinders are gilded. If the equality of the weight has been disturbed, it is restored by inverting the lighter cylinder for a short time again in the gold-bath.

After the weighing pans of the balance have been removed, a beaker with freshly distilled water is put under each end of the beam; and by the aid of thin platinum wire an aluminum cylinder is fastened on each of the hangers of the beam, so that the cylinders are immersed in the water. After a time sufficient for the cylinders to acquire the temperature of the water, and after ascertaining that the temperature of the latter is exactly the same in both beakers, it is observed whether the weights of the cylinders in water are equal or not. If there should be any slight difference, the lighter cylinder is transferred to the left side and

the difference of the weights made up by a piece of thin platinum wire, to be attached to the hanger of the left-hand beam. The same operation is repeated with the third cylinder, after the removal of the cylinder on the left-hand side.

If this is satisfactorily accomplished, the beakers with water are removed and, when the temperature of the room is nearly  $0^{\circ}$ , two tumblers are procured, with ground rims and ground covers, the latter each containing in the center a hole of about five-tenths cm. diameter, and near the rim a hole to admit a thermometer, which has a cylindrical vessel, and is graduated on the stem. The one tumbler is filled partly with fused calcium chloride and caustic lime or potash; the other is nearly filled with cold distilled water. The first tumbler is put under the hanger of the left beam, and the other under that of the right-hand beam. After a time, sufficient for the cylinders and the water to acquire the temperature of the surrounding air ( $t^{\circ}$ ), the weight is read off. It is:

$x$  = the weight of each aluminum cylinder in grams.

$y$  = the volume of each aluminum cylinder in cc.

$z$  = difference of weights, if one is immersed in pure air, the other in pure water.

$z_1$  = the same, reduced to the vacuum.

$a$  = specific gravity of pure water at  $t^{\circ}$  (air thermometer) and  $h$  barometric pressure.

$b$  = specific gravity of dry air at  $t^{\circ}$  (air thermometer), and  $h$  barometric pressure.

$b_1$  = specific gravity of the air at  $t^{\circ}$  (air thermometer) in the balance case.

$c$  = specific gravity of the gilded weights at  $t^{\circ}$  (platinum weights are to be preferred).

Then  $x + ay - z_1 = x + by$ ,

or  $\frac{z_1}{a - b} = y \dots \dots \dots (1)$

Further  $z_1 = z + z \frac{b_1}{c}$

or  $z_1 = \frac{z(c + b_1)}{c} \dots \dots \dots (2)$

If this value of  $z_1$  is substituted in equation 1, we get :

$y = \frac{z(c+b_1)}{c(a-b)}$ . The same operation is repeated at about 25°, 50°, and 75°. In the latter two instances the temperatures of the water and air will, of course, differ considerably. From the values obtained, a table is calculated of the volumes of the aluminum cylinders for each degree of the air thermometer from 0° to 100°.

To ascertain the specific gravity of the air in the balance case at the time, when it is intended to determine the specific gravity of a liquid, the tumbler with pure water and thermometer is put under the left hanger of the balance, the cylinders hooked to the hangers of the beam, the one immersed in the water, the other in the air. After a time, sufficient for the water to have acquired the temperature of the air, the weight is read off. We have then :

$$x + ay - z_1 = x + b_1y; \text{ or } a - \frac{z(c+b_1)}{cy} = b_1.$$

Substituting for  $b_1$  on the left side repeatedly the value  $a - \frac{z(c+b_1)}{cy}$ , we get :

$$a - \frac{z}{y} - \frac{za}{cy} + \frac{z^2(c+a)}{c^2y^2} - \frac{z^3(c+a)}{c^3y^3} + \frac{z^4(c+a)}{c^4y^4} - \frac{z^5}{c^5y^5} = b_1;$$

*i. e.*, the specific gravity of the air, if that of the water is assumed to be 1.00. If  $t^\circ$  is not 4.1° C.,  $b_1$  has to be divided by  $a$  and the formula becomes :

$$1 + \frac{\left(\frac{z^2(c+a)}{c^2y^2} + \frac{z^4(c+a)}{c^4y^4}\right) - \left(\frac{z}{y} + \frac{za}{cy} + \frac{z^3(c+a)}{c^3y^3} + \frac{z^5}{c^5y^5}\right)}{a} = b_1$$

The aluminum cylinder on the right hand is thence removed and the tumblers with the liquid to be examined, into which the third cylinder and a thermometer had already been immersed, is put in its place, the cylinder hooked to the hanger, and the weight ascertained.

If the specific gravity of a liquid at a high temperature is to be determined (*i. e.*, the expansion coefficient), a hole directly underneath the hanger of the right-hand beam passes through the upper and lower bottoms of the balance case and also through the table. Through this hole passes a platinum wire

connected with the one cylinder hanging in the beaker, containing the liquid, on a water-bath over a Bunsen burner.

When the liquid in the beaker has about the desired temperature, the lamp is extinguished and the weight of the cylinder ascertained.

Now the thermometer is read off again and the weight again ascertained. If the temperature has risen in the meantime the operation is repeated, till the weight is less than at the first reading. The averages of all temperatures and of all weights are taken and used for the computation.

### A SHORT STUDY OF METHODS FOR THE ESTIMATION OF SULPHUR IN COAL.<sup>1</sup>

BY G. L. HEATH.

Received June 15, 1898.

AS a manufacturer's requirements with regard to certain metallurgical processes become more exacting from year to year, the determination of sulphur in the fuel must become more important. The interest taken in this subject is evidenced by the appointment of the committee from the society, who have just made their preliminary report. The writer has been led, as a matter of interest, to communicate some experimental work upon the determination of sulphur.

There has been a little controversy, or doubt, as to the relative accuracy of the two "sintering" or "ignition" methods in general use as compared with each other, or with the old method of fusion with sodium carbonate and potassium nitrate. It must be assumed and understood that the following work was done rather to study methods and show precautions necessary, than to obtain close check results. This remark explains a discrepancy in results on one coal of very high sulphur content, since the methods which will now be described as used by the writer, were purposely not modified to suit that special case.

#### 1. THE "FUSION" METHOD.

This is so well given in the text-books with so little variation that full description is unnecessary.<sup>2</sup> Blair's modifications used.

<sup>1</sup> Read at the meeting of the New York Section, June 3, 1898.

<sup>2</sup> Blair's Analysis of Iron, 1886, p. 245.



In our experience, much care must be taken to dehydrate, by evaporation with acid, the silicic acid which dissolves in the solution of the fused alkali. This renders the process too slow for technical work.

## 2. ESCHKA'S METHOD.<sup>1</sup>

*a.* One gram of powdered coal is intimately mixed with one gram of pure magnesium oxide and one-half gram sodium carbonate, and heated with the flame of a large (eight-ounce) alcohol lamp in a platinum dish of about 100 cc. capacity. A dish is much to be preferred to a narrow crucible, since it offers a better exposure of the coal to the air, and prevents excessive heat and dry distillation in the interior of the mass.

The mixture is frequently stirred with a platinum wire and the heat is raised very slowly, especially so with very soft coals. The flame, which is kept in motion and barely touches the dish at first until strong glowing has ceased, is increased gradually until, in fifteen minutes, the bottom of the dish is at a low red heat. When the carbon has burned away the mass is transferred to a No. 2 Griffin beaker and boiled five minutes with 100 cc. of distilled water and some oxidizing agent.

Fifteen cc. of saturated bromine water, as recommended by Mack and by Handy, is the purest and most efficient reagent to use, safer than the plan of adding ammonium nitrate during ignition. The hot liquid is then passed through a washed filter and the residue washed with hot water until the total volume is approximately 200 cc. The filtrate is then acidified strongly with hydrochloric acid, boiled until the free bromine is driven off, and sufficient hot solution of barium chloride added to insure the precipitation of all the sulphuric acid as barium sulphate, which is settled, filtered, and ignited.

*b.* Fresenius recommends that the ignited mixture be boiled directly in bromohydrochloric acid, which will dissolve all the sulphur in high coals, but loads the solution with salts and possibly silica.

*c.* The modification, recently published, involving the use of silver oxide, does not seem to offer any advantage whatever

<sup>1</sup> *Chem. News*, 21, 261; *J. Anal. Appl. Chem.*, 6, 611.

over the other methods using inexpensive material, and is not included in the table.

### 3. HUNDESHAGEN'S METHOD.<sup>1</sup>

It is a familiar fact that this modification differs from Eschka's only in the substitution of potassium carbonate for sodium carbonate. The advocate of the first salt claimed that sodium carbonate did not retain all the organic sulphur from certain Bohemian brown coals.

J. O. Handy,<sup>2</sup> of Pittsburg, presented tests from which he deduced a conclusion in opposition to that of Hundeshagen, but he does not appear to have tested the particular class of coals specified by the latter chemist. The writer has, accordingly, experimented with a variety of samples, including Bohemian brown coal, and has experimented also with a few variations in the details of procedure. Part of the foreign samples were procured from the Michigan College of Mines, and a fine specimen of the Bohemian article from Prof. Lattimore, of the University of Rochester.

The proximate analyses were carried out as usual with the author, according to Blair's<sup>3</sup> modification of Heinrich's method. Blank analyses for the sulphur in reagents were also carried through. This is the more necessary, as I have sometimes met with goods labelled by importers "strictly C. P.," which were rather impure.

An inquiry, in one case, elicited the statement from a clerk that his house labelled articles C. P. to fill orders for the highest grade, even if they were only a common grade on the market at the time. The American firm of Baker & Adamson, it is but just to state, has furnished the purest chemicals for fuel analysis that we could obtain anywhere.

### 4 AND 5. WILEY'S AND CARIUS' METHODS.

I have had no experience with the Wiley and Carius methods, which are not so much used, as such, in America.

### 6. WET METHOD OF CALVERT.

The "wet method" of Calvert<sup>4</sup> is useful for the scientific inves-

<sup>1</sup> *Chem. Ztg.*, 15, 1070; also *J. Anal. Appl. Chem.*, 5, 385.

<sup>2</sup> *J. Anal. Appl. Chem.*, 6, 116.

<sup>3</sup> Blair's Analysis of Iron, 1888, p. 243.

<sup>4</sup> *Chem. News*, 24, 26; also Watts' Dictionary of Chemistry.

## ESTIMATION OF SULPHUR IN COAL.

TABLE I.  
PROXIMATE ANALYSES OF THE DOMESTIC AND FOREIGN COALS. SULPHUR INCLUDED IN FIGURES—NOT DEDUCTED  
FROM CARBON.

No.	Variety.	Special characteristics.	Locality.	Per cent. mois- ture at 105° C.	Per cent. vola- tile and com- bustible mat- ter.	Per cent. fixed carbon.	Per cent. of ash.
1	Bituminous	clean lump	Ohio, U. S.	0.72	37.15	57.01	5.12
2	"	fine slack of	"	0.78	30.72	54.92	13.58
3	Anthracite	clean lump	Penna., U. S.	2.47	3.00	88.80	5.73
4	"	"	"	2.95	3.23	86.95	6.87
5	Bituminous	"	W. Va., U. S.	0.62	31.28	62.07	6.03
6	"	fine slack of	"	0.75	29.64	62.75	6.86
7	Gray, soft	friable	Rhenish Prussia	2.72	23.03	6.41	67.84
8	Bituminous, soft	a little shaly	Pleasant Hill, Iowa, U. S.	1.26	43.72	45.65	9.37
8B	"	weathered shaly sample	"	1.85	42.90	45.97	9.28
9	Black, jet	lustrous, vitreous	Spain or Bohemia	2.83	38.70	49.46	9.01
10	Kerosene shale	grayish brown, woody pieces	N. S. Wales	0.07	82.05	5.81	2.07
11	Carmel	grayish	Hartley Vale, Blue Mts., N. S. Wales	0.07	81.37	5.32	13.24
12	Lignite	brown lump	Kosten, Bohemia	8.17	44.14	39.14	8.55

tigation of the forms in which the sulphur exists in fuel, but is unsuitable for technical work.

#### 7. FAHLBERG-ILES PROCESS.<sup>1</sup>

The modified Fahlberg-Iles process of fusion with caustic potash in a silver crucible is correct, but is open to a strong objection, which does not affect either Eschka's or Hundeshagen's methods. It is necessary to heat slowly over an alcohol lamp to complete fusion, and the silica is thereby rendered soluble, but must be subsequently dehydrated by tedious evaporation. Accordingly, I have confined this work to the two most rapid technical methods, including a few results by complete fusion for comparison.

TABLE II.  
EXPERIMENTAL SULPHUR DETERMINATIONS. PER CENT. OF SULPHUR FOUND.

No. of sample.	Treated in 100 cc. platinum dish.	Oxidized by bromine water.			
		Eschka's method.	Hundeshagen's method.	Oxidized with hydrogen peroxide. Eschka's method.	Fusion method with sodium carbonate and potassium nitrate in crucible.
1	Ignited.....	1.375	1.364	1.372	....
2	" .....	2.203	2.197	....	....
3	" .....	0.529	0.551	0.545	....
4	" .....	....	0.530	0.521 <sup>2</sup>	....
5	" .....	1.063	1.068	....	....
6	" .....	1.637	1.635	....	....
7	" .....	1.480	1.540	1.760(c) <sup>3</sup>	....
	" .....			1.690(d)	
8A	" .....	4.95	4.99	....	4.97(e)
	" .....		4.74		
8B <sup>4</sup>	" .....	4.76	4.69(g)	....	....
	" .....	(h)4.80	4.88(m)	....	4.89(f)
9	" .....	0.201	0.203	....	....
10	" .....	0.364	0.375	....	....
11A	" .....	0.43	0.41	....	....
11B	" .....	0.30	0.33	....	....
12	" .....	0.966	0.967	0.923	0.968
	" .....	(h)0.907		0.983(d) <sup>3</sup>	

<sup>1</sup> Furman's Manual of Assaying, 1895, p. 88.

<sup>2</sup> Hundeshagen's method used in this case.

<sup>3</sup> Oxidized with sodium peroxide.

<sup>4</sup> This is sample 8A weathered by two years' exposure of the powder to air.

7(c). Two grams sodium peroxide added during the ignition.

7(d) and 12(d). Two grams of sodium peroxide added to the aqueous solution of the ignited residue, and boiled. The 7(c)(d) results are too high owing to dissolved silica.

8(e). The fused mass was directly dissolved in dilute acid, and then evaporated to dryness, taken up again with dilute hydrochloric acid, and filtered.

8(f). The fused mass was boiled with water only, and the solution filtered, then acidified with hydrochloric acid, and evaporated to dryness in order to dehydrate silica. (g). Ignited very quickly at strong heat in dish. (h). Ignited this quickly in crucible. See No. 8B, Hundeshagen's method, also No. 12. 8B, 11, and 12 were made with a compact variety of magnesium oxide, and in analysis 8B not quite all the sulphates could be extracted in five minutes boiling with water.

8(m). Ignited mass dissolved directly in bromohydrochloric acid.

From the foregoing experimental analyses in addition to regular work, considerable information has been secured concerning the effect of variation in the small details of the standard methods, and the precautions to be observed in their use, which might be summed up for discussion, as follows :

1. I cannot confirm the statement of Hundeshagen that Eschka's mixture does not retain all the sulphur from certain coals, and as far as my experience goes must agree with Handy's opinion with one qualification.

2. Rapid heating with magnesium oxide and alkaline carbonate in a deep crucible may be made to give a little lower results than slow heating in a shallow dish with such a coal as No. 12 (brown coal), but with coal No. 11 (jet) it was necessary to heat very slowly, even in a dish, so as to avoid too great a heat, which might allow dry distillation of combined sulphur without complete oxidation.

Hundeshagen's loss, which he attributed to the inability of sodium carbonate to retain all the sulphur of brown coals, may be due to rapid heating in a crucible of the sodium carbonate mixture, which is also more dusty than one of coal, magnesia, and potassium carbonate.

3. The "sintering" methods, when performed with good

judgment, agree closely with the results obtained by fusion of the coal with sodium carbonate and potassium nitrate.

4. If the "fusion method" is used, or sodium peroxide employed as an oxidizing agent, great care must be taken to dehydrate all silica by evaporation with hydrochloric acid.

Some chemists direct that the fused mass should be boiled with water and filtered before acidification with hydrochloric acid.<sup>1</sup> Other authorities state that the fused mass is to be dissolved directly in dilute acid.

The first procedure is to be preferred as the iron oxide and insoluble matters are removed at once by the filtration of an aqueous solution of the fusion.

5. The purest and most efficient reagent to complete the oxidation of sulphur compounds in the aqueous solution of the ignited residue of the "ignition" methods is a saturated solution of bromine in water. The use of hydrogen peroxide involves the testing of every bottle of the reagent for the very variable quantity of sulphuric acid it always contains. If this impurity is determined by a blank analysis and the amount deducted in the proper manner, the results obtained by its use are quite satisfactory (see 1, 3, 4, 12).

If sodium peroxide is added at first to a mixture of coal and magnesium oxide, the action is too violent. If added when the coal is nearly burned, the mass, nevertheless, balls on heating and some soluble sodium silicate appears to be formed by the heating or during subsequent aqueous extraction, and the barium sulphate will be a little impure unless silica is dehydrated by evaporation. Refer to coal analysis No. 7 (c) and (d).

In the writer's experience, no reagent gives as good results as the bromine water.

6. The five minutes' boiling of the ignited residue of coal ash, magnesium oxide, and carbonates with water (as generally prescribed by the authors) is sufficient to convert all the insoluble sulphates of lime, iron, etc., unless these substances are present in considerable quantity, or unless the magnesium oxide is a compact, heavy sample, as employed with No. 8B and No. 12. Under these circumstances the boiling and extraction of the ignited residue with water should be prolonged

<sup>1</sup> Blair's Iron Analysis; see also Stillman's Engineering Chemistry, p. 20.

for, say, an additional period of ten minutes—a precaution not alluded to by chemical authors, but a necessary one.

The two following experiments were made in order to show that this precaution must be taken with fuels, especially weathered coals, carrying a large amount of either iron or calcium sulphates.

TABLE III.

Sample No. 13.	Barium sulphate. Gram.
Taken, 1+ grams coal, yielding.....	0.0295
Added 0.1869 gram C. P. calcium sulphate, yielding..	0.3202
Total.....	0.3507
Result of ignition, boiling five minutes with 100 cc. water + 15 cc. bromine and washing (blank allowed for).....	0.2615
Deficiency =	0.0882
Sample No. 14.	Barium sulphate. Gram.
Taken, 1+ grams coal, yielding.....	0.0325
Added 0.4070 gram weathered ferrous sulphate con- taining the equivalent of.....	0.3490
Total.....	0.3815
Result of ignition, boiling five minutes with 100 cc. water + 15 cc. bromine and washing (blank allowed for).....	0.3509
Deficiency =	0.0306

As far as my experience goes, the methods, irrespectively of Eschka and Hundeshagen, which involve a simple ignition, at low temperature, with a sulphur absorbent, are far preferable as rapid operations, suitable for technical work, to any plan necessitating a complete fusion with a consequent solution of silica. The two preferred methods will uniformly furnish accurate results, within usual limits of error in sampling, if the operator will only exercise a little judgment in certain cases.

With anthracite coal and coke there is no liability to error. With softer fuels, especially lignites, the materials should be especially well ground, well mixed, and stirred during the ignition in an open dish and if the proximate analysis and the appearance of the ash, indicates that the coal contains a large percentage (over three per cent.) of sulphur as pyrites (or calcium sulphate in the ash), the boiling and washing should be continued for a longer time, and the washed residue finally dissolved in acid, and qualitatively tested by itself.

## BOOKS RECEIVED.

Lighting by Acetylene—Generators, Burners, and Electric Furnaces. By William E. Gibbs, M.E. New York: D. Van Nostrand Co. 1898. 141 pp. 66 illustrations. Price, \$1.50.

A Laboratory Guide in Qualitative Chemical Analysis. By H. L. Wells, M.A. First Edition. New York: John Wiley & Sons. London: Chapman & Hall, Ltd. 1898. vii + 154 pp. Price, \$1.50.

A Short Course in Inorganic Qualitative Analysis for Engineering Students. By J. S. C. Wells, Ph.D., Instructor in Analytical Chemistry, Columbia University. First Edition. New York: John Wiley & Sons. London: Chapman & Hall, Ltd. 1898. vi+294 pp. Price, \$1.50.

Review and Bibliography of the Metallic Carbides. By J. A. Mathews, M.S., M.A., F.C.S. 32 pp. 1898. Smithsonian Institution, Washington, D.C.

The Value of Experiments on the Metabolism of Matter and Energy. By C. F. Langworthy, Ph.D. 17 pp. [Reprinted from Experiment Station Record, Vol. IX, No. 11.]

A Brief Course in Qualitative Analysis. By Ernest A. Congdon, Ph.B., F.C.S. 62 pp. New York: Henry Holt & Co. 1898. 62 pp. Price, 60 cents.

Nutrition Investigations at the University of Tennessee in 1896 and 1897. By Chas. E. Wait, Ph.D., F.C.S. Bulletin No. 53, U. S. Department of Agriculture, Office of Experiment Stations, Washington, D.C. 1898. 46 pp.

A Study of Lettuces. The Results of a Varietal Test of Lettuces for the Benefit of the Lettuce Growers of North Carolina. Bulletin No. 147. June 6, 1898. 8 pp. North Carolina Agricultural Experiment Station, Raleigh, N. C.

Digestion Experiments. Pasteurization of Milk. Bulletin No. 48. June 8, 1898. 30 pp. The North Carolina Agricultural Experiment Station, Raleigh, N. C.

Milk as Food. Farmers' Bulletin No. 74. U. S. Department of Agriculture, Washington, D. C. 39 pp.

Traité D'Analyse des Substances Minérales. Par Adolphe Carnot. Tome Premier.—Méthodes Générales D'Analyse, Qualitative et Quantitative. Paris: V<sup>re</sup> Ch. Dunod, Editeur. 1898. 992 pp.

Nutrition Investigations in New Mexico in 1897. By Arthur Goss, M.S. U. S. Department of Agriculture, Office of Experiment Stations, Washington, D. C. 20 pp.

Proceedings of the Fourteenth Annual Convention of the Association of Official Agricultural Chemists held at Washington, D. C., October 26, 27, and 28, 1897. Edited by Harvey W. Wiley, Secretary of the Association. Bulletin No. 51, U. S. Department of Agriculture, Division of Chemistry, Washington, D. C. 169 pp.



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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF PURDUE UNIVERSITY.]

## NOTES ON TAKA-DIASTASE.

BY W. E. STONE AND H. E. WRIGHT.

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THERE has recently come into notice, chiefly through its industrial applications, a starch-saccharifying enzyme of apparently unusual value. This substance, called taka-dias-tase, has been in use in Japan for an indefinite time in the production of alcoholic beverages in much the same capacity as that for which we employ malt. Its introduction to America is due to Mr. Jokichi Takamine, who for some years has been occupied in furthering its application in the distilling industry in the United States. Pharmaceutical preparations of this enzyme intended for the relief of amylaceous indigestion, are also on the market. So far as the writers are informed neither the material itself nor its action on starch has been much studied from the purely scientific side or, if such investigations have been made, they have not been generally published. It seemed a matter of interest, therefore, to endeavor to secure definite information regarding such a valuable and interesting material.

Mr. Takamine has recently described<sup>1</sup> the patented method for preparing the material, a résumé of which will be appropriate here. Taka-dias-tase is, so far as known, somewhat similar to malt-dias-tase in its chemical character; *viz.*, a highly

<sup>1</sup> *Am. J. Pharm.*, 70, No. 3; *J. Soc. Chem. Ind.*, 17, No. 2.

nitrogenous substance, readily soluble in water and dependent upon certain conditions of temperature for its maximum activity. Its action is also affected by alkalies and acids. It is produced as the result of the growth of a species of mould (*Eurotium Oryzae* Ahlberg), upon rice, maize, wheat bran, etc. For its production, as at present practiced in this country, wheat bran is steamed and, after cooling, is sown with the spores of the fungus. After twenty-four hours in culture-rooms at a temperature of about 25° C. the fungus growth becomes visible. In forty or fifty hours the content in diastatic material has reached the maximum and further growth of the fungus is checked by cooling. The material, now consisting of the bran felted together with fungus mycelium, is called "taka-koji."

It may be mixed with grain or starchy materials in the same manner as malt is used, and, like malt, will speedily convert the starch into fermentable sugars. An aqueous extract of the mass may be used for a similar purpose. For the preparation of a pure product, which however is not necessary for ordinary industrial purposes, the aqueous extract is concentrated by evaporation and on the addition of alcohol the diastatic substance may be precipitated as a yellowish powder, easily soluble in water, of stable keeping qualities and possessed of an unusual power of converting starch into sugar. The medicinal preparation above mentioned is obtained in this way and represents a fairly pure form of the diastatic principle. This bears the name of "taka-diastase."

This paper presents the results of some observations upon the action of taka-diastase upon starch as compared with the ordinary diastase of malt.

For the purposes of this comparison, taka-diastase was employed which was kindly furnished by the makers, Messrs. Parke, Davis & Co., of Detroit, Mich. The malt-diastase was prepared in the laboratory by digesting fresh pale malt with water at room temperature during three or four hours, filtering and adding to the clear filtrate two volumes of strong alcohol. The flocculent precipitate was collected, pressed dry, and finally dried in desiccators over sulphuric acid.

A series of experiments was carried out in which pure potato starch, which had been changed to paste by boiling, was sub-

jected to the action of the two sorts of diastase. Three methods were employed to determine the degree to which the starch had been changed; *viz.*, first, the iodine test; second, the optical behavior of the solution; third, the determination of the actual amounts of sugar produced.

In every case care was taken to preserve uniform conditions except as specified below.

1. Comparative action of the two kinds of diastase on potato starch as indicated by the iodine test.

*a.* Four samples of starch of one-half gram each were boiled with fifty cc. of water each. To two were added 0.05 gram malt-diestase each and they were kept at 60° C. throughout the test. To the other two were added 0.05 gram taka-diestase and these were kept at 40° C. throughout the test. At fixed intervals the solutions were tested with iodine for the presence of starch, in the following manner: Three drops of the solution were removed to a white test plate and were mixed with one drop of standard aqueous iodine solution containing one and a half grams potassium iodide and eight-tenths gram iodine in one liter. The least trace of starch is indicated under these conditions by a blue or greenish tint or as the starch is passing through some of the preliminary stages of conversion the tint will be more or less violet or purple. In this and other experiments the duplicate samples were found to agree very closely in their behavior.

The results of the observations were as follows:

End of six minutes: Malt-diestase, no perceptible change; taka-diestase, deep violet color.

End of twelve minutes: Malt-diestase, reddish brown; taka-diestase, violet to reddish.

End of eighteen minutes: Malt-diestase, light brown or yellow due to iodine solution; starch reaction had disappeared; taka-diestase, light violet or reddish.

End of forty-five minutes: Taka-diestase, light violet tint.

End of sixty minutes: Taka-diestase, light greenish-blue tint, evidently containing small traces of unchanged starch.

*b.* The proportions of starch to diastase were increased, in other respects the conditions remaining the same as in "*a*". Four samples of starch of one gram each, converted to paste by

boiling with fifty cc. of water, received diastase of each kind as above.

End of six minutes : Malt-diastase, deep violet ; taka-diastase, deep reddish violet.

End of twelve minutes : Malt-diastase, reddish violet ; taka-diastase, deep reddish violet.

End of eighteen minutes : Malt-diastase, reddish brown ; taka-diastase, light reddish violet.

End of twenty-seven minutes : Malt-diastase, light brown, no starch reaction ; taka-diastase, slightly reddish violet.

End of six hours : Taka-diastase, still a bluish green color showing small amounts of unchanged starch.

c. The proportions of starch to diastase were again increased. Four samples of two and a half grams each of starch were converted to paste in 250 cc. of water and received respectively 0.05 gram malt- or taka-diastase.

End of six minutes : Malt-diastase, no perceptible change ; taka-diastase, deep reddish violet.

End of twelve minutes : Malt-diastase, deep reddish violet ; taka-diastase, deep reddish violet.

End of forty-five minutes : Malt-diastase, brownish yellow color, no further starch reaction ; taka-diastase, light violet or greenish tint.

End of twelve hours : Taka-diastase, still showed the bluish-green tint.

d. The amounts of diastase were diminished. Four samples of starch of 1.875 grams each in forty cc. of water, received respectively 0.025 gram of taka- or malt-diastase.

End of six minutes : Malt-diastase, deep blue, little or no change ; taka-diastase, deep reddish violet.

End of twelve minutes : Malt-diastase, reddish brown ; taka-diastase, deep reddish violet.

End of twenty-four minutes : Malt-diastase, yellowish brown color, no starch reacting ; taka-diastase, reddish violet.

End of forty-five minutes : Taka-diastase, still gives a violet tint.

e. Four samples of starch of two and a half grams each in 250 cc. water with 0.025 gram respectively of malt- or taka-diastase.

End of six minutes : Malt-diastrase, no change ; taka-diastrase, deep reddish-violet.

End of twelve minutes : Malt-diastrase, deep reddish brown ; taka-diastrase, deep reddish brown.

End of twenty-four minutes : Malt-diastrase, yellowish brown, no starch reaction ; taka-diastrase, deep reddish brown.

End of sixteen hours : Taka-diastrase, still gave a bluish drab color.

In every case it was apparent to the observer that the effect of the taka-diastrase was more rapid at the outset, as indicated by the almost immediate change from the typical blue of the starch iodine compound to reddish and violet tints. It was generally noticeable also that the taka-diastrase liquefied the starch paste very rapidly, more so than the malt-diastrase. On the other hand, the complete conversion of the starch into forms which no longer gave color reactions with iodine was effected much earlier by the malt-diastrase, while the taka-diastrase scarcely attained this result after several hours.

2. Comparative action of the two kinds of diastase on potato starch as shown by optical tests.

The different conversion products of starch exhibit varying degrees of optical activity. The dextrans possess a high specific rotation usually stated as approximately  $190^{\circ}$ . Maltose has the specific rotation  $130^{\circ}$ – $140^{\circ}$ , while the ultimate conversion product, dextrose, has the specific rotation  $52.5^{\circ}$ .

In considering the action of diastase, however, maltose may be regarded as the ultimate product, and Brown and Morris have pointed out<sup>1</sup> that the optical behavior of a solution of the products of diastatic action on starch paste, is that of a mixture of maltose and dextrose. A determination, therefore, of the specific rotation of such a solution gives information regarding the degree of conversion of the starch. The degree of completeness of the change from starch through dextrans of high specific rotation to maltose of a lower rotatory power will be indicated by a diminution of the specific rotation. A few qualitative observations along this line were made as follows :

Eight samples of starch of equal weight were converted to paste by boiling in equal amounts of water ; to each of four were added

<sup>1</sup> *Chem. News*, 71, 123.

0.05 gram malt-diastase and to the other four 0.05 gram taka-diastase each. These samples were kept respectively at 60° and 40° C. At regular intervals one of each series was withdrawn, heated quickly to boiling to check further action of the diastase, cooled, and made up to a volume of 100 cc. The specific rotation was then determined in a Laurent polarimeter with sodium light. Two series of experiments were made in this way, using different amounts of starch.

## a.

One-half gram starch in 100 cc. water.

0.05 gram of diastase.

Malt-diastase at 60° C.			Taka-diastase at 40° C.	
Time. Hours.	Observed rotation.	Specific rotation.	Observed rotation.	Specific rotation.
$\frac{1}{4}$	1°20'	133°20'	1°15'	125°
$\frac{1}{2}$	1°19'	131°40'	1°13'	121°40'
1	1°19'	131°40'	1°9'	115°
2	1°19'	131°40'	1°7'	111°40'

## b.

One gram starch in 100 cc. water.

0.05 gram of diastase.

Malt-diastase at 60° C.			Taka-diastase at 40° C.	
Time. Hours.	Observed rotation.	Specific rotation.	Observed rotation.	Specific rotation.
$\frac{1}{4}$			2°47'	139°20'
$\frac{1}{2}$	2°57'	147°30'	2°43'	135°50'
1	2°45'	137°30'	2°29'	124°10'
2	2°47'	139°20'	2°27'	122°30'

The products of the action of taka-diastase were in all cases of lower specific rotation than those from malt-diastase, indicating a more rapid change to maltose.

3. Comparative action of the two kinds of diastase on potato starch as indicated by the amount of sugar formed.

The most practical as well as most conclusive test of the relative degree to which starch has been converted by diastatic action is that of actually determining the amount of sugar formed under comparative conditions. This has been done as follows :

Several equal samples of the starch were boiled with equal volumes of water to change into paste, were cooled to the proper temperature, and received respectively given amounts of one or

the other diastase. At the expiration of a given time one sample of each kind was withdrawn, boiled to check the action of the diastase, cooled, and filled up to definite volume. The amount of sugar present was determined by the method described by Defren.<sup>1</sup>

It is believed that these results form a very good basis for comparing the actual efficiency of the two enzymes for a given time.

## a.

One-half gram starch. 100 cc. water. 0.05 gram diastase.

Malt-diastase at 60° C.				Taka-diastase at 40° C.		
Time.	Cupric oxide from 10 cc.	Maltose. Mg.	Total mal- tose from 5 grams starch. Mg.	Cupric oxide from 10 cc.	Maltose. Mg.	Total mal- tose from 5 grams starch. Mg.
Hours.						
$\frac{1}{4}$	39.5	29.0	290	61.4	44.3	443
$\frac{1}{2}$	41.1	29.7	297	63.9	46.5	465
1	40.7	29.7	297	65.8	47.9	479
2	40.2	29.0	290	73.0	53.0	530

## b.

One gram starch. 100 cc. water. 0.05 gram diastase.

Malt-diastase at 60° C.				Taka-diastase at 40° C.		
Time.	Cupric oxide from 10 cc.	Maltose. Mg.	Total mal- tose from 1 gram starch. Mg.	Cupric oxide from 10 cc.	Maltose. Mg.	Total mal- tose from 1 gram starch. Mg.
Hours.						
$\frac{1}{4}$	71.4	51.6	516	84.5	61.8	618
$\frac{1}{2}$	84.7	61.8	618	99.6	72.8	728
1	75.5	55.2	552	120.1	87.4	874
2	85.5	61.8	618	143.6	105.0	1050

These results show that for a given short time the actual saccharifying power of the taka-diastase is decidedly superior to the malt-diastase.

4. The use of taka-diastase as an analytical reagent for the determination of starch.

Malt-diastase has come to be most favorably looked upon as an agent for the selective removal and analytical determination of starch occurring in grains and vegetable materials, associated with other carbohydrates. One drawback to its common use is its unstable character in the isolated form, since it is well known

<sup>1</sup> This Journal, 18, 749.

that preparations of diastase rapidly deteriorate and lose their value. On this account the practice is to freshly prepare aqueous infusions of malt for immediate use in starch determination. Such infusions, however, always contain sugar, which being added to the analytical sample necessitates a subsequent correction. The use of malt-dia $\dot{t}$ astase in any form therefore as an analytical reagent is more or less tedious and renders welcome any substitute which would avoid these objections and at the same time act as an efficient starch solvent. Taka-dia $\dot{t}$ astase has seemed a promising substance for this purpose, although the qualitative tests described under "r" indicate that it does not readily effect complete conversion of starch under the conditions stated.

The following experiment upon materials commonly presented for starch determinations is instructive :

One gram each of air-dried, finely ground wheat, maize, and potato were heated to the boiling-point during thirty minutes with fifty cc. of water. After cooling to 60° C., ten cc. of malt infusion were added to each and the temperature was carefully maintained as above. To each of a similar series prepared in the same way was added 0.05 gram and to each of another similar series 0.1 gram of taka-dia $\dot{t}$ astase : these samples were kept at 40° C. At the expiration of four and one-half hours all were subjected to the iodine test for starch. In those treated with malt infusion all traces of starch had disappeared from the potato while the wheat and maize still showed slight traces of starch under the microscope. In those treated with taka-dia $\dot{t}$ astase, all, without exception, showed an abundance of unchanged starch, nor was there apparently any sharp distinction between the samples of the same material receiving different amounts of the dia $\dot{t}$ astase.

After seven hours the samples treated with malt-dia $\dot{t}$ astase gave no further indication of starch. But all of those treated with taka-dia $\dot{t}$ astase gave pronounced starch reactions. Additional treatment during twelve hours at ordinary temperature did not suffice to remove all of the starch from the latter samples.

Evidently these results were unfavorable to the employment of taka-dia $\dot{t}$ astase as a reagent but a quantitative comparison was



made as follows: Duplicate, two-gram samples of air-dried, ground wheat were weighed and gelatinized by boiling thirty minutes with 100 cc. of water. To one was added twenty cc. of a malt infusion made by digesting five grams of malt in fifty cc. of water three hours at ordinary temperature; this sample was then kept at 60° C. To the other duplicate was added 0.05 gram taka-diastrase and the temperature kept at 40° C.

After four hours the solutions were filtered. The residue from the wheat treated with malt infusion proved to be free from starch when examined under the microscope after treatment with iodine solution. The wheat treated with taka-diastrase was slightly stained blue when treated with iodine. The filtrates received each ten cc. concentrated hydrochloric acid and were heated in boiling water during one hour. After cooling, neutralizing, and making up to volume, the amount of sugar in each was determined by titration with Fehling's solution and the results calculated to starch in the original samples of wheat.

The treatment with malt infusion gave 55.46 per cent. of starch. The treatment with taka-diastrase gave 52.94 per cent. of starch.

This result agrees wholly with the qualitative experiments previously made and indicates that under the stated conditions taka-diastrase is not adapted for use in the quantitative determination of starch. It is nevertheless possible that some modification of these conditions or of the material itself may lead to more satisfactory conclusions as the result of some future investigation.

It is certain, however, that in gross industrial operations the cheapness and stability of taka-koji and taka-diastrase will commend it while its ability to convert a very large proportion of the starch present in a grain into sugar within a very short time should render it a very valuable substitute for malt. The application of taka-diastrase as an aid to starch digestion is doubtless of high value by reason of its convenience, its notable saccharifying power, and its permanent keeping qualities.

## THE ACTION OF ORGANIC ACIDS UPON NITRILS.<sup>1</sup>

BY JOHN ALEXANDER MATHEWS.

Received July 7, 1898.

THE action of organic acids upon nitrils has been the subject of a number of investigations which have been reported from this laboratory at intervals during the past seven years. The nitrils and acids employed in the various experiments have been made to react under the influence of elevated temperature and pressure in sealed tubes. In nearly every instance a few drops of acetic anhydride have been added to the mixtures of acids and nitrils to insure anhydrous conditions within the tubes. This precaution is believed to increase the yield of the principal products of the reaction. The reaction between acetic acid and acetonitril, whereby Gautier found diacetamid to be produced,<sup>2</sup> suggested to Colby the idea of trying parallel reactions between other acids and nitrils. Colby and Dodge<sup>3</sup> experimented with a large number of monobasic acids and mononitrils of both the fatty and the aromatic series. Their results show that under conditions of heat and pressure :

- I. Fatty nitrils and fatty acids yield secondary amids.
  - II. Fatty nitrils and aromatic acids yield fatty acids and aromatic nitrils.
  - III. Aromatic nitrils and fatty acids give mixed secondary amids.
  - IV. Aromatic nitrils and aromatic acids give secondary amids. One exception was noted under the fourth head by these authors.
- Not so much work has been done upon dibasic acids. Miller<sup>4</sup> and Seldner<sup>5</sup> worked with fatty dibasic acids, the former with succinic and the latter with glutaric acid. They proved that the imids of these acids result under three different conditions. From

### I. Dibasic acid and acetonitril.

<sup>1</sup> Read at the meeting of the New York Section, May 6, 1898.

<sup>2</sup> *Ztschr. anal. Chem.*, 1869, p. 127, or *Compt. rend.*, 60, 1255.

<sup>3</sup> *Am. Chem. J.*, 13, 1.

<sup>4</sup> This Journal, 16, 443.

<sup>5</sup> *Am. Chem. J.*, 17, 532.

II. Dinitril and acetic acid, and

III. Equal molecules of the dibasic acid and its nitril.

Two years ago the author published his first experiments upon aromatic dibasic acids. Phthalic acid was first tried and its imid resulted by heating it with propionitril. In the following pages are given results obtained recently along the same line of experimentation. This work may be grouped under two heads. First, experiments with monobasic acids, simple and substituted; second, experiments with aromatic, polybasic acids.

## PART I.

### UPON THE ACTION OF FATTY NITRILS ON MONOBASIC AROMATIC ACIDS, WITH A PRELIMINARY NOTE ON MALONIMID.

Before describing the experiments upon aromatic acids which compose the main part of this investigation, a few words upon some attempts to prepare the unknown imid of malonic acid may not be out of place, since in these attempts the methods employed were the same as those used in making the imids of the bibasic aromatic acids.

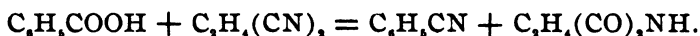
*Malonic Acid and Ethylene Cyanide.*—Two tubes containing equal molecules of malonic acid and ethylene cyanide were made by Miller in 1893. The first tube, when heated, exploded at 196° C. The second one was heated at 150° C. for five and one-half hours. This tube was set aside and when examined by me recently it was found that the contents were liquid and brown. Very strong outward pressure was noticed upon unsealing. Succinimid was found but no malonimid seems to have been produced. Malonic acid loses part of its carbon dioxide readily by heating, and for this reason it was thought better to use malonitril and treat it with glacial acetic acid. This method was unsatisfactory, too, for almost complete decomposition took place by heating. As throwing some light upon the question of the rearrangement of cyan acids to give imids, the next experiments were made upon cyanacetic acid. This acid was heated to 190° in benzol medium. There was strong pressure upon opening and the contents of the tube were evaporated upon the water-bath to drive off the benzol. The residue was extracted with absolute alcohol. This solution was treated with boneblack and by evap-

oration nearly to dryness and long standing a small amount of crystalline material separated. This was pressed and dried and recrystallized. It was soluble in acetone, ether, alcohol, and water, and almost insoluble in benzol. Its melting-point was  $115^{\circ}\text{C}$ . It gave a nitrogen test and was neutral in its reaction with litmus paper. By boiling with potassium hydroxide solution, acidifying and evaporating to dryness, and extracting with absolute alcohol, an acid was obtained melting at  $130^{\circ}$ , very soluble in water and alcohol. This seems to be malonic acid. It seems probable, therefore, that malonimid was produced by the rearrangement of the cyanacetic acid. Not enough of this supposed imid has as yet been obtained to make a thorough investigation, but the same material was obtained from two tubes made up and heated at different times and its further study will be interesting.

*Benzoic Acid and Ethylene Cyanide.*—Two sealed tubes containing ethylene cyanide and benzoic acids and a drop or two of acetic anhydride were prepared. The first contained equal molecules and the second contained two parts of acid to one part of nitril. Both were heated seven hours at  $145^{\circ}\text{C}$ . and then five and a half hours at  $195^{\circ}\text{C}$ . The contents were then black and semi-solid and crystalline. In the first tube benzonitril was found. The contents of the tube were treated with weak sodium carbonate solution and then evaporated to dryness and extracted several times with ether. The operations thus far described were carried out by Dr. E. H. Miller, in 1893. The ether extract gave a white crystalline solid upon evaporation. This residue was very soluble in acetone. After recrystallization from water and twice from acetone, succinimid, melting at  $124^{\circ}\text{C}$ ., was obtained in characteristic crystals. These were tested for nitrogen and it was found.

The second tube contained originally three grams of ethylene cyanide and 9.15 grams of benzoic acid; *i. e.*, two molecules of acid to one of nitril. No pressure was observed upon opening. A strong odor of benzonitril was at once apparent. The tube contents were liquid at the temperature of a hot water-bath and were poured into dilute sodium carbonate solution. From results obtained by Colby and Dodge and by Miller, it was

thought that this tube might contain benzoic acid, ethylene cyanide, benzonitril, succinic acid, succinimid, and dibenzamid. Dibenzamid and succinic acid were not found. Colby and Dodge showed that by heating together benzoic acid and acetonitril at  $250^{\circ}$ – $260^{\circ}$  C. there was formed principally benzonitril and acetic acid. At about the same temperature benzonitril and benzoic acid combine to give dibenzamid. In our tube probably the temperature had not been carried high enough to produce this condensation. The primary reaction which seems to have taken place in both tubes is :



The second tube was examined as follows : Upon pouring the contents into sodium carbonate solution three and one-half cc. of black liquid material separated at the bottom. This was drawn off by means of a separatory funnel and showed to be benzonitril. It was distilled with steam, separated from the water, partly dried by evaporation upon a water-bath, and then with small fragments of calcium chloride. The once purified product boiled at  $188^{\circ}$  (uncorr.). The boiling-point of benzonitril is given as  $191^{\circ}$  C.

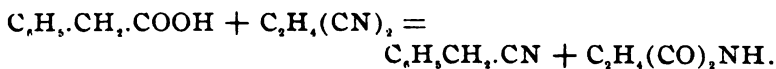
The sodium carbonate solution was evaporated to dryness and extracted with ether and then with water. The ether extract gave a residue upon evaporation which was succinimid. Recrystallized from acetone it gave oblong, colorless crystals (melting-point  $125^{\circ}$  C.).

The water extract above mentioned by acidifying with hydrochloric acid gave a bulky precipitate. This, filtered off, washed, and dried, melted at  $117.5^{\circ}$ . It was unchanged benzoic acid. Recrystallized from hot water, large plates were deposited (melting-point  $120^{\circ}$  C.). These crystals are sublimable at the temperature of boiling water. 2.75 grams of benzoic acid were recovered, which is also about the amount of benzonitril produced. After the ether and water extractions of the original tube contents, a large, charred, carbonaceous residue and a little tarry matter, believed to be partly ethylene cyanide, remained.

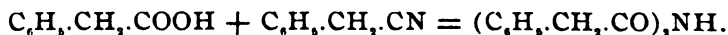
In Miller's dissertation upon succinimid are reported a number of attempts to prepare  $\beta$ -cyanpropionic acid in sufficient quantities to try whether it could be made to rearrange into its

isomer, succinimid. It seems to me that these two experiments point to the formation of  $\beta$ -cyanpropionic acid as an intermediate product. Either it must be considered that the carboxyls of the benzoic acid change places with both nitril groups of one-half of the ethylene cyanide or with one of the nitril groups forming  $\beta$ -cyanpropionic acid, which rearranges into succinimid. Of course, if the first assumption is the correct one, the succinic acid formed would react with the unchanged ethylene cyanide and two molecules of succinimid would result as shown by Miller. It seems probable that had succinic acid been formed in either of these experiments some of it would have been found, for these reactions are not often complete. On the other hand, if  $\beta$ -cyanpropionic acid were the intermediate product we should not expect, because of its well-known instability, to find it withstanding a temperature of  $195^{\circ}$  unchanged. Only about one gram of succinimid was produced and this fact, together with the large amounts of decomposition-product, seems to strengthen the second assumption in regard to the course of the reaction.

*Phenylacetic Acid and Ethylene Cyanide.*—Two tubes, the first containing equal molecules of phenylacetic acid and the second two molecules of acid to one of nitril, were prepared by Miller in 1893. Both tubes were heated for six hours at  $150^{\circ}$  C. The contents were then black and semi-fluid. Not much outward pressure was noticed upon opening. These tubes were set aside and not examined until 1898. The reaction in tube I seems to be:



Phenylacetamid was also found in this tube and its presence cannot be explained except by the presence of some water in the tube which reacted upon the phenylacetoneitril. The reaction of tube II was primarily the same as in I. The excess of phenylacetic acid then reacted with the phenylacetoneitril and produced diphenyldiacetamid:



No phenylacetamid was found in this experiment, but some phenylacetic acid was recovered.

Tube I was examined as follows: The contents were extracted with warm water. A black, oily residue was left. This proved to be impure phenylacetonitril. The water extraction was of a light yellow color and, by cooling, it gave crystals. These were flat plates melting at  $155^{\circ}\text{C}$ . They were found to contain nitrogen and, by boiling with hydrochloric acid and cooling, crystals of phenylacetic acid were deposited (melting-point  $76^{\circ}\text{C}$ .). A second crop of the crystals melting at  $155^{\circ}$  was obtained by concentrating the mother-liquor. These crystals were phenylacetamid. By evaporating the second mother-liquor nearly to dryness succinimid was found. This, recrystallized from acetone, melted at  $124^{\circ}\text{C}$ .

Tube II was examined in about the same way. The water extract by cooling gave no phenylacetamid. Upon concentration some phenylacetic acid separated and later succinimid was found. The black oily residue from the water extraction was soluble in hot alcohol. It was treated with boneblack and then upon cooling, needle crystals melting at  $190^{\circ}\text{C}$ . were obtained. These were recrystallized and deposited as slender filament-like needles, melting at  $192^{\circ}$ . They were insoluble in water and seemed to be diphenyldiacetamid, described by Colby and Dodge. The alcohol solution, after filtering off the diphenyldiacetamid, was distilled. The high-boiling fraction was caught separately and dried. The boiling-point of the benzyl cyanide thus obtained was  $230^{\circ}\text{C}$ .

It will be noticed that these results are parallel to those obtained with experiments with benzoic acid. The two series of experiments form a connecting link between the work of Colby and Dodge upon monobasic acids and their nitrils, and the work of Miller upon succinimid, and serve to confirm in several points the reported results of these chemists.

*Salicylic Acid and Acetonitril.*—Equal molecules of salicylic acid and acetonitril were heated five hours at  $195^{\circ}$ – $200^{\circ}\text{C}$ . No reaction seems to have taken place, unchanged salicylic acid being the only solid product. This experiment repeated at  $215^{\circ}$ – $230^{\circ}$  always gave a reddish liquid. Great pressure was noted in these last experiments and carbon dioxide was the principal gas evolved. Phenol was shown to be present in every case. No other products were identified. The tube contents were partly

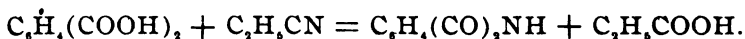
soluble in water and the insoluble portion consisted of a sticky, thick liquid substance. The water solution by cooling gave a few clusters of crystals, melting at  $137^{\circ}$ – $138^{\circ}$ , after recrystallization. These gave no nitrogen reaction. The first reaction seems, then, to result in the formation of phenol, and unidentified products mentioned above do not result by any action of a nitril upon an acid. The investigation was, therefore, discontinued for the present and will be resumed later.

*Anthranilic Acid and Acetonitril.*—Anthranilic acid and acetonitril were heated together in equal molecules for five hours at  $220^{\circ}$ – $230^{\circ}$  C. Very strong pressure was observed upon opening the tubes and the gases evolved consisted mainly of carbon dioxide. The tube contents were evaporated to dryness upon a water-bath. The black residue was almost entirely soluble in hot water. This solution upon cooling gave fine needle-like crystals (melting-point  $230^{\circ}$  C.). These, treated with boneblack and recrystallized, melt at  $232^{\circ}$  C. and may be sublimed. By boiling them with strong hydrochloric acid and cooling, long needles result, which do not melt at  $280^{\circ}$  C. but sublime. This material was not identified nor were the few drops of liquid (boiling-point  $240^{\circ}$ ), which were isolated in one of the experiments. This liquid did not give a test for anilin with bleach solution but gave a deep brown color when so treated. On account of the partial decomposition taking place within the tubes, no further investigations upon anthranilic acid and acetonitril were made, but the reaction will be made the subject of future study.

## PART II.

### UPON THE ACTION OF FATTY NITRILS UPON AROMATIC POLY-BASIC ACIDS.

*Phthalic Acid and Propionitril.*—In a number of reactions which I have tried phthalimid resulted. The first of these experiments was made in 1896.<sup>1</sup> This series of experiments is explained by the following reaction :



The tubes were made up containing both one and two molecules of nitril to one molecule of phthalic acid. The best

<sup>1</sup> This Journal, 18, 679.



results, so far as the production of phthalimid was concerned, were obtained by heating equal molecules of the reagents at  $180^{\circ}$ – $200^{\circ}$  for a period of five and a half hours. The yield was ninety-two per cent. of the theoretical. The reaction seems to be practically completed in three and a half hours, for one tube heated thus yielded eighty-eight per cent. The crystalline product in these tubes was washed with a little dilute sodium carbonate solution to remove phthalic and propionic acids and any nitril remaining. The crystals remaining melted at  $228^{\circ}$  C. Portions recrystallized from alcohol, acetic acid, and alcohol with the addition of boneblack, melted a little higher,  $229.5^{\circ}$ – $230^{\circ}$  C. These crystals gave off ammonia by boiling with potassium hydroxide. By standing with concentrated ammonium hydroxide they were converted into phthalamid, microscopic needles melting at  $217.5^{\circ}$  (uncorrected). The amid is decomposed by boiling, giving off ammonia gas, and phthalimid crystallizes out again upon cooling.

*Phthalic Acid and Ethylene Cyanide.*—Equal molecules of phthalic acid and ethylene cyanide were heated together. Two tubes received four hours' heating at  $220^{\circ}$ – $223^{\circ}$ . Upon opening, strong outward pressure was noticed, and the contents of the tubes were black and charred. Thinking that succinimid might be present, the tube contents were extracted with water. This solution upon evaporation gave a small amount of material, very soluble in methyl or ethyl alcohol and acetone, difficultly soluble in benzol. It crystallized in needles (melting-point  $165^{\circ}$ – $167^{\circ}$ ), and gave nitrogen test by boiling with alkali. By boiling with hydrochloric acid, crystals were obtained which melted above  $200^{\circ}$  with decomposition. The residue, after cooling, melted at  $127^{\circ}$  and sublimed in fine needles. This seems to be phthalic acid. The hydrochloric acid solution, after filtering off the above crystals, was shaken up with ether. The ether solution, by evaporation, gave a small residue (melting-point  $183^{\circ}$ – $185^{\circ}$ ), which corresponds with succinic acid and when boiled with sulphuric acid and alcohol gave an odor of succinic ester. The solution, after extracting with ether, was evaporated to dryness, dissolved in a little water and a platinic chloride test made for ammonia. The precipitate which was obtained was tested to make sure that no fixed alkalies were present. Unfortunately,

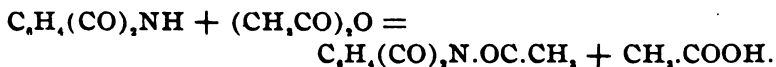
the amount of this substance produced was too small for further investigation or analysis. The above tests, however, would indicate that the compound might be a double imid of phthalic and succinic acids. The second tube contained also a little of this material, having the same properties as before, but its melting-point was found to be a little higher,  $170^{\circ}\text{C}$ .

In a third tube, run as nearly as possible like these two, for the purpose of obtaining enough of this peculiar compound to analyze, none of it was found. In tube I no succinimid was found, but there was a great deal of phthalimid. In tubes II and III succinimid and phthalimid were found, the former in very small quantities. In all the tubes was found considerable black, charred, insoluble residue.

Tube IV was heated to  $200^{\circ}$  for five hours. Upon examination succinimid, phthalimid, and unchanged phthalic acid were found. In tube II the contents were moist and an attempt was made to filter off the solid portion by using a hot water funnel. The funnel was covered with a watch-glass and the vapors which arose from the funnel deposited upon the cover glass, white crystals, which upon drying and recrystallizing, proved to be succinimid. The reaction which works then to some extent in these experiments is :



III. *Phthalic Anhydride and Acetonitril*.—When acetic anhydride and acetonitril are heated at  $200^{\circ}$  there is found triacetamid,  $(\text{CH}_3\text{CO})_3\text{N}$ . To see if a similar reaction would take place between phthalic anhydride and acetonitril giving acetylphthalimid, these reagents were heated together in equal molecules, and also with excess of nitril, but in neither case was acetylphthalimid formed. According to Aschan<sup>1</sup> acetylphthalimid is produced when phthalimid is boiled for several hours with acetic anhydride in a flask with return condenser, thus :



Acetylphthalimid is easily decomposed by hot water or alcohol and by cold alkali. Aschan notes that the imid hydrogen does not readily submit to replacement by acid radicals.

<sup>1</sup> *Ber. d. chem. Ges.*, 19, 1400.

In my experiments tube I, containing equal molecules, was heated four hours at  $145^{\circ}\text{C}$ ., and then four and a half hours at  $195^{\circ}$ – $200^{\circ}\text{C}$ . Upon examining the tube contents phthalic anhydride and phthalimid were found. The latter should not have resulted had the reagents used not contained moisture. Tube II received the same treatment as I and four hours additional at  $225^{\circ}$ – $235^{\circ}\text{C}$ . It showed no apparent change over tube I and was unsealed, more nitril added, and after resealing it was heated again at  $200^{\circ}$ – $210^{\circ}$  for five hours. Phthalimid was again found, together with acetic acid and unchanged phthalic anhydride. Tube III was made up as the other two except that the nitril used was twice distilled over phosphorus pentoxide. In this tube no reaction took place, except that a little imid was again found. The reaction expected seems therefore not to have worked under the conditions presented.

*Terephthalic Acid and Propionitril.*—Under the same conditions which gave phthalimid from *o*-phthalic acid and propionitril, no reaction takes place with *p*-phthalic acid, neither is any reaction obtained at a much higher temperature,  $260^{\circ}\text{C}$ . The tube contents, after heating, are completely soluble in dilute carbonate solution, except that at the higher temperatures a little tarry substance may remain. The solid contents do not give a nitrogen test and *p*-phthalic acid is recovered quantitatively by acidifying the sodium carbonate solution with hydrochloric acid.

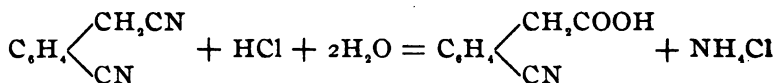
*Homophthalic Acid and Acetonitril.*—The experiments with homophthalic acid and acetonitril, looking to the production of homophthalimid, were not entirely successful because of the small quantity of homophthalic acid obtainable. In but one instance was any product found resembling homophthalimid. This is rather surprising, inasmuch as the ammonium salt of this acid gives an imid by heating, and every other acid whose imid results in this way and that has been tried by our nitril reaction has given an imid. After five hours' heating of equal molecules of homophthalic acid and acetonitril at  $190^{\circ}\text{C}$ . and extracting the tube contents with carbonate solution, a small residue remained. Upon dissolving this in hot acetic acid and cooling, crystals were obtained which do not entirely melt, but darken, and give off a brown liquid at  $230^{\circ}\text{C}$ ., leaving a charred residue. The crystals contain no nitrogen. The mother-liquor

from them by concentration gave a few crystals which contain nitrogen and melt, after drying between filter-papers, at  $215^{\circ}$ . A third crop of crystals filtered off, washed, and dried, were light brown, contained nitrogen, and melt at  $230^{\circ}$ – $232^{\circ}$ , darkening before melting. These answer to the description of homophthalimid. The amount of this product was very small and nothing like it was isolated in two subsequent similarly conducted experiments. In all of them, however, the material not containing nitrogen and decomposing above  $230^{\circ}$  into a brown liquid and charred residue was found.

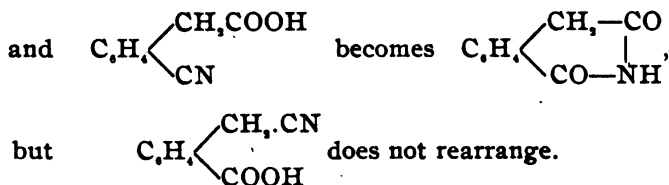
A peculiar compound very insoluble in cold alcohol and acetic acid and soluble in ammonia, was found. Its melting-point was indefinite, but by heating it left a residue infusible at  $285^{\circ}$  C. It crystallizes in fine filament-like crystals, which are snow-white and pack down to a spongy, felt-like mass of a texture which makes it scarcely visible upon the filter-paper. It contains no nitrogen and not enough of it was obtained to analyze.

Cyan-*o*-toluic acid did not rearrange by heating under pressure in benzol at  $190^{\circ}$  C. to yield its isomer, homophthalimid. In this regard it differs from *o*-cyanbenzoic acid, which so readily changes into phthalimid. An ether solution of the tube contents in one of these experiments gave a few long needle-shaped crystals, melting at  $182^{\circ}$  C. They contained nitrogen but were not identified.

Gabriel<sup>1</sup> states that cyan-*o*-toluic acid does not rearrange to give an imid but does not mention under what conditions the experiment was tried to produce this change. He concludes that when the cyanogen group is on the ring, rearrangements may be expected as was just mentioned of *o*-cyanbenzoic acid. In proof of this he shows that by acting upon orthocyanbenzyl cyanide with fuming hydrochloric acid at  $100^{\circ}$  for one hour homophthalimid is produced. He explains this by considering that the cyan group of the side chain is more reactive than the cyan group on the ring, hence *o*-cyanphenylacetic acid is first formed and this rearranges to give homophthalimid. That is:



<sup>1</sup> Ber. d. chem. Ges., 20, 2502.



*Diphenic Acid and Acetonitril.*—Diphenic acid and acetonitril in equal molecular proportions were heated together in a sealed tube for six hours, the temperatures increasing gradually from  $225^\circ$  to  $240^\circ\text{C}$ . A strong odor of acetic acid was noticed when the tube was opened. The contents were treated with cold dilute sodium carbonate solution and the solid crystalline residue was thrown upon a filter and washed with water. This product was dissolved in warm chloroform and from this solution long needles melting at  $217^\circ\text{C}$ . (uncorrected) were obtained. These crystals may be sublimed and were proved to be diphenimid by tests to be mentioned later. Recrystallized and treated with boneblack, long, colorless crystals, melting at  $217.5^\circ\text{C}$ ., were obtained from alcoholic solution. There has been a difference of opinion among chemists as to the melting-point of diphenimid and diphenamid, respectively. Wegerhoff states that the imid and amid both melt at  $215^\circ$ . Graebe and Aubin give the melting-point of the imid as  $219^\circ$ – $220^\circ$  and of the amid as  $208^\circ$ – $209^\circ$ .<sup>1</sup> Later Wegerhoff<sup>2</sup> gives figures differing from his own statement in the *Berichte*, 21, 2356; viz.,  $212^\circ$ – $213^\circ$  and  $217^\circ$  for the amid and imid respectively. There is an obvious reason for different results upon the amid because it decomposes readily, losing ammonia, and gives the imid. My own experience confirms Wegerhoff's figures last mentioned. In determining the melting-point of diphenamid different results were obtained depending upon the rapidity with which it is heated to the point of fusion. By slow heating decomposition is gradual; the melting-point tube becomes clouded and complete fusion may not take place before  $217^\circ$ , while by rapid heating no apparent decomposition takes place and the crystals melt at  $212^\circ$ – $213^\circ\text{C}$ .

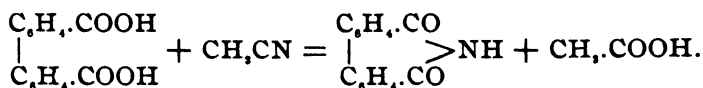
To confirm my results, I tested the diphenimid as follows: By standing with cold, concentrated ammonia, hexagonal crys-

<sup>1</sup> *Ann. Chem.* (Liebig), 247, 270.  
<sup>2</sup> *Ibid.*, 252, 16.

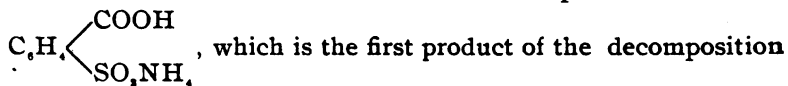
tals separate out. These melt at  $212^{\circ}$ – $213^{\circ}$ , give off ammonia by heating, and are apparently diphenamid. The separation of the crystals takes place almost immediately if the ammonia solution is warmed. By boiling diphenimid with concentrated potassium hydroxide solution, ammonia is evolved. The first product of the action of potassium hydroxide, however, is this :



By acidifying with hydrochloric acid and cooling after the brief action of potassium hydroxide solution, colorless plate-like crystals of diphenamic acid were deposited, melting at  $190^{\circ}$ – $191^{\circ}$  C. Diphenimid is almost entirely insoluble in boiling water. The yield of diphenimid by the reaction tried was about ninety per cent. of the theoretical, estimated upon the product once crystallized from chloroform. The reaction which accounts for this production of diphenimid is :

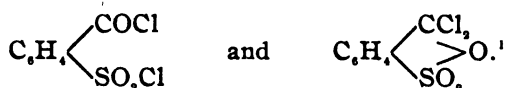


*o*-Sulphobenzoic Acid and Acetonitril.—The *o*-sulphobenzoic acid used in this series of experiments was made by Remsen's method from saccharin.<sup>1</sup> Briefly, the method is to decompose saccharin by boiling with strong hydrochloric acid. This solution is evaporated to dryness and cold water added. This dissolves the acid ammonium salt of *o*-sulphobenzoic acid,



of saccharin with hydrochloric acid. Any *p*-sulphaminebenzoic acid which the saccharin may have contained remains undissolved. The water solution, by evaporation and cooling, gives large diamond-shaped crystals of the ammonium salt. These are treated with phosphorus pentachloride. The mixture becomes semi-fluid, owing to the production of oxychloride of phosphorus and sulphobenzodichloride,

<sup>1</sup> *Am. Chem. J.*, 11, 332.



The reaction-product is poured in ice-water and a yellow oily layer of the acid chlorides separates and is thoroughly washed and then decomposed by boiling with water, producing *o*-sulphobenzoic acid. This crystallizes from a concentrated aqueous solution with four molecules of water of crystallization. To obtain the anhydrous acid, it was heated at 130°–135° several times, alternately cooling it in a vacuum desiccator over sulphuric acid. The last traces of water are hard to remove and at a temperature a little above that necessary to keep the sulphobenzoic acid liquid, it begins to darken.

An error seems to have crept into the literature of this compound regarding its melting-point. It is stated in nearly all the chemistries that have been consulted that *o*-sulphobenzoic acid melts at 250°. The melting-point is 68° for the hydrated acid and about 130° for the anhydrous. The acid ammonium salt mentioned above melts between 250°–260°, and this compound, when first made and described, was thought to be the free acid.<sup>2</sup>

The sulphobenzoic acid thus prepared was heated with acetonitril in equal molecules at 165°–170° for five hours. The first set of tubes examined exhibited no pressure upon unsealing and showed a light brown sirupy material in which were seen transparent crystals. The tube contents were treated with cold, absolute alcohol. The sirupy part dissolved readily and the crystals remained. They were soluble in hot absolute alcohol and were crystallized from this medium. They then appeared as large, diamond-shaped plates, melting at about 260°. They gave a nitrogen test and were acid in reaction and taste. They seemed to be the acid ammonium salt of sulphobenzoic acid, and their presence is explained by the fact that the first sulphobenzoic acid prepared was not completely anhydrous. A portion of it, further heated at 135° and then treated with the nitril as before, gave only the sirupy material. The second lot of sulphobenzoic acid prepared gave, when heated with the nitril, no residue insoluble in cold absolute alcohol. Some of the dia-

<sup>1</sup> Remsen : *Ibid.*, 17, 309.

<sup>2</sup> Brackett, Hayes : *Ibid.*, 9, 405.

mond-shaped crystals were boiled with potassium hydroxide and evaporated to dryness. The residue, by treatment with phosphorus pentachloride, gave a yellow oily substance resembling *o*-benzosulphodichloride. This disappeared by adding ammonia, probably with the formation of an amid.

The sirupy portion in alcohol solution, treated with boneblack and evaporated to dryness, became crystalline by cooling. When redissolved in alcohol and set aside to crystallize, minute, indistinct, white crystals separated. They give a faint acid reaction to litmus and phenolphthalein, no reaction with methyl orange. They contain nitrogen and sulphur, are very soluble in water and alcohol, insoluble in ether. They do not form an ammonium salt by evaporating to dryness with ammonia water and seem to be unchanged by this treatment. They possess no sweet taste. The first product of this kind examined melted at  $220^{\circ}$ – $221^{\circ}$ . This is the same melting-point as that given for saccharin. The product from the second set of experiments melts at  $225^{\circ}$ . I have reason to believe that this was a purer product than the first material examined. It softens before melting and the melting-point tube becomes clouded. It is not sweet after melting and begins to darken a little above its melting-point.

From the parallel with phthalic acid it was expected that these experiments might give saccharin,  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown SO_2 \end{smallmatrix} NH$ ,

or possibly its isomer *o*-sulphobenzonitril,  $C_6H_4 \begin{smallmatrix} \diagup CN \\ \diagdown SO_2H \end{smallmatrix}$  The

product is not the latter compound because its solution does not decompose carbonates and an ammonium salt corresponding to that described by Remsen<sup>1</sup> could not be formed. Its different solubilities and lack of sweet taste show that it is not saccharin, but a quantitative determination of nitrogen shows it to be isomeric with it, and it may therefore be the unsymmetrical sulphobenz-

imid,  $C_6H_4 \begin{smallmatrix} \diagup CNH \\ \diagdown SO_2 \end{smallmatrix} O$ . Still another isomer is possible, pseudo-saccharine, whose derivatives of this type are known,

<sup>1</sup> *Am. Chem. J.*, 18, 819.



$$\text{C}_6\text{H}_5 \begin{array}{c} \diagup \text{COR} \\ \diagdown \text{SO}_2 \end{array} \text{N}.$$
 More thorough investigation will be made of our

compound to establish its constitution. The determination of nitrogen resulted as follows :

	1.	2.
Weight of sample.....	0.3187	0.3333
Weight of nitrogen .....	0.0232	0.0252
Per cent. nitrogen .....	7.28	7.56
“ “ calculated for $\text{C}_7\text{H}_5\text{O}_2\text{SN}$ .		7.65

The presence of the acid ammonium salt of sulphobenzoic acid in our first tubes is really a confirmation of the fact that the main reaction has given an imid, for by the action of water we

should get,  $\text{C}_6\text{H}_5 \begin{array}{c} \diagup \text{COOH} \\ \diagdown \text{SO}_2\text{NH}_4 \end{array}$ , just as is the case when saccharin

is acted upon by strong hydrochloric acid, whereas if *o*-sulphobenzonitril had been formed, it would have given *o*-sulphobenzamid by the action of water under pressure.

*Mellitic Acid and Acetonitril*.—A tube containing mellitic acid (one molecule) and acetonitril (three molecules) with a few drops of acetic anhydride, was heated four hours at  $265^\circ$ – $275^\circ$  C. The contents of the tube were very dark-colored and were extracted with water and washed on the filter until the washings were no longer acid. The insoluble residue being still dark was extracted with alcohol and with dilute sodium carbonate solution. Very little material dissolved by this treatment, but this residue was lighter colored. Nitrogen was tested for in this residue and its presence detected.

The sodium carbonate washings, by acidifying, gave a very dark and mostly flocculent precipitate. This gave the euchronic acid test. The final residue, after the extraction mentioned above, was insoluble in hydrochloric acid, but dissolved in sulphuric. When the acid solution was poured into water and let stand a very fine precipitate appeared. This was paramid and still retained its brown tint.

This experiment was repeated at a lower temperature, heating for three hours at  $180^\circ$ – $200^\circ$ , and three hours at  $225^\circ$ – $235^\circ$  C. The tube contents were only slightly discolored. About

ninety per cent. of the paramid was found after extractions with hot water and with very dilute ammonia had been made. The insoluble residue dissolves in strong ammonia and gives a precipitate which seems to be euchronamic acid upon the addition of hydrochloric acid. This precipitate, as was stated by Wöhler, yields the same color reactions as euchronic acid.

The color imparted to a solution by euchron is very unstable. It disappears instantly by shaking with access of air and in a test-tube containing a solution of a very small amount of euchronic acid a color may appear at the bottom when the zinc is added while the top of the solution remains colorless. The purple-red color obtained in an alkaline solution behaves in the same way, but is a more delicate test for the presence of euchronic acid. The red color is produced whether the zinc is added first to the water solution and then ammonia added, or the zinc may be added to an ammoniacal solution of euchronic or euchronamic acid. If paramid and zinc dust be shaken together in water, no color reaction takes place, but by adding ammonia a red color appears, showing the production of euchronamic acid.

Schwartz<sup>1</sup> found very few reducing agents available for producing euchron. In the course of this investigation it was discovered that aluminum amalgam gives the red color. The reaction progresses slowly, the aluminum foil being first colored red, before any color is imparted to the solution.

In the examination of the contents of tube II it was found that the original water extraction, upon cooling, gave a crystalline precipitate. This was filtered off and found to be readily soluble in hot water, from which it could be precipitated by adding nitric acid. The crystals thus obtained were square prisms of euchronic acid. In working with mixtures containing euchronic acid one notices that nearly every solution obtained during the examination will give euchron by adding zinc dust, provided the solution tested is not strongly acid with inorganic acid. The color reaction in alkaline solution is so delicate that one part of euchronic acid in more than 100,000 parts of solvent may be detected. Under such conditions the

<sup>1</sup> *Ann. Chem.* (Liebig). 66, 46.

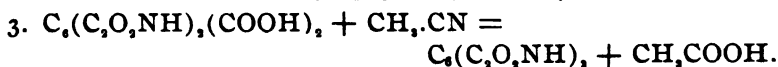
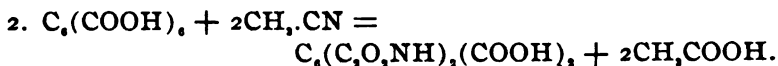
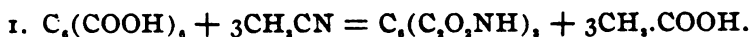
color develops slowly and the solution should be kept corked during the test.

It was thought by heating together equal molecules of mellitic acid and acetonitril that mellitmonimid would result. A tube containing these reagents and a few drops of acetic anhydride were heated during four and one-half hours at  $215^{\circ}$ – $220^{\circ}$ . The tube contents were white and all soluble in water. No monimid was found, only euchronic acid and unchanged mellitic acid being produced. A repetition of this experiment verified these results, a large amount of euchronic acid having been found. Euchronic acid crystallizes from water in the form of six-sided plates and in long prisms from an acid solution.

Another attempt to prepare mellitmonimid was made by employing the two-thirds neutralized mellitic acid. A standard solution of sodium hydroxide was used and four of the six carboxyls were saturated. The solution was evaporated to dryness and dehydrated. The acid salt remaining was heated with acetonitril for several hours at  $230^{\circ}$ , and even at  $290^{\circ}$  no nitrogen was found to have entered the mellitic compound. This argues rather that the sodium atoms have not entered consecutively than that there is any reason why a monimid should not exist.

The conversion of paramid into euchronamic acid would indicate that Wöhler's euchronic acid is an ortho compound. In confirmation of this the following experiment should be recorded. A quantity of euchronic acid was dried at  $200^{\circ}$ . The crystals do not lose their form at this temperature but become opaque and dull. The dried euchronic acid was heated with an excess of acetonitril for three and a half hours at  $223^{\circ}$  C. Paramid was not produced and the euchronic acid was recovered and tested. As the paramid of my previous experiments had been made at a higher temperature than  $223^{\circ}$ , the experiment was repeated at  $240^{\circ}$ – $260^{\circ}$  C. After three hours' heating the contents were examined and paramid found. The reaction was not complete, for some euchronic acid was recovered. This seems to show that the carboxyls of this euchronic acid are in the ortho position. The paramid produced in these experiments was always dark-colored and no means of purification has been found. The euchronic acid, however, was always white or a very pale yel-

low tint. The reactions which have been found to take place in this series of experiments are :



Another series of experiments was tried upon the partly neutralized mellitic acid, two objects being in view ; *i. e.*, the determination of the order in which the carboxyls combine with sodium, and second, to prepare the other two possible imids. Only partial success was obtained along both these lines. If large quantities of mellitic acid could be used, so that the partially neutralized salts could be isolated and crystallized, there is no doubt that both of these objects would be attained. Two tubes containing the tetra acid disodium salt  $[\text{C}_6(\text{COO})_2\text{H}_2\text{Na}_2]$  were heated with acetonitril, two molecules of the latter to each molecule of the acid salt. They received five hours' heating at  $225^\circ\text{--}240^\circ$ . Very slight pressure was noted upon opening. The contents were washed with ether several times and with ninety-five per cent. alcohol. The ether extract contained acetic acid. The solid contents were soluble in water and by acidifying thin needle-like crystals came down. Recrystallized from water they came down as thin plates. These crystals give the euchron test but are very different from the euchronic acid previously prepared. They consist of large thin plates, imperfectly formed and twinning somewhat. They give an acid reaction and do not melt below  $295^\circ\text{C}$ ., but lose water of crystallization. They undergo no other change at this temperature and after heating give the euchron test as before. To further prove that they were not *o*-euchronic acid they were heated for five hours at  $240^\circ\text{--}260^\circ$  with propionitril. No paramid was produced. The *p*-euchronic acid recovered was recrystallized from water and gave very thin six-sided plates. The first two sodium atoms seem to have entered at 1 and 4. From two tubes, in which what was thought to be the triacid trisodium salt had been used and heated with nitril as before, no monimid was isolated. It may be that the saturation with sodium hydroxide gives a mix-

ture of compounds, for euchronic acid was obtained from this experiment. Its analysis resulted as follows :

	H <sub>2</sub> O. Per cent.	N. Per cent.
C <sub>12</sub> O <sub>8</sub> H <sub>4</sub> N <sub>2</sub> (+ 2H <sub>2</sub> O).....	10.6	9.31
Found.....	10.0	9.13

The figures for nitrogen are based upon the anhydrous euchronic acid. The previous experiments upon the tetrasodium salt of mellitic acid show that the sodium atoms enter at 1, 2, 4, and 5.

#### CONCLUSIONS.

In the foregoing experiments it has been shown that

I. Cyanacetic acid under certain conditions appears to rearrange to yield its isomer malonimid.

II. Benzoic acid and ethylene cyanide give benzonitril and succinimid.

III. Phenylacetic acid and ethylene cyanide give phenylacetonitril and succinimid. As a secondary product phenylacetic acid and phenylacetoneitril give diphenyldiacetamid.

IV. In II and III it seems probable that  $\beta$ -cyanpropionic acid is an intermediate product and rearranges to give succinimid, and that in general, when an imid is produced by this reaction, it may be considered as resulting from an intermediate cyanacid.

V. The substituted monobasic acids, salicylic and anthranilic, give no similar results on account of the decompositions they undergo by heating.

VI. Phthalimid results from phthalic acid and propionitril, and phthalimid and succinimid result from phthalic acid and ethylene cyanide.

VII. Phthalic anhydride and acetonitril do not react under the conditions presented.

VIII. Terephthalic acid and propionitril do not react under the conditions presented.

IX. Homophthalimid is not readily formed from homophthalic acid and a nitril. It does not result by a rearrangement of cyan-*o*-toluic acid.

X. Diphenimid results in nearly theoretical amounts from diphenic acid and acetonitril.

XI. *o*-Sulphobenzoic acid and acetonitril yield a compound isomeric with saccharin which may be the unsymmetrical *o*-sulphobenzimid.

XII. By varying the conditions three of the four possible imids of mellitic acid were produced by heating this acid with acetonitril. The *p*-euchronic acid is a new compound; *o*-euchronic acid and paramid were known but have resulted also by our nitril reaction. It has been shown that aluminum amalgam can be used to give the euchron test.

To sum up then briefly, I believe I have made three new imids; *viz.*, malonimid, *p*-euchronic acid, and an imid of sulphobenzoic acid. The known imids of succinic, phthalic, homophthalic, diphenic, and mellitic acids have been made by a new method. The conclusions of Colby and Dodge, stated in the introduction, have been confirmed and the first method used by Miller and Seldner for producing fatty imids has been found applicable for producing aromatic imids. The widest general conclusion to be drawn from the work of these earlier investigators of the action of nitrils upon acids and from my own work is that when acids and nitrils are heated together they tend to form disubstituted ammonia compounds, secondary amids from monobasic acids and nitrils, imids from dibasic acids and nitrils.

ORGANIC LABORATORY, HAVEMEYER HALL,  
COLUMBIA UNIVERSITY.

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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 2.]

### THE ACTION OF METALLIC THIOCYANATES UPON ALIPHATIC CHLORHYDRINS.<sup>1</sup>

BY WILBER DWIGHT ENGLE.

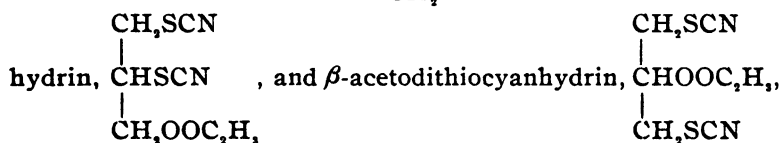
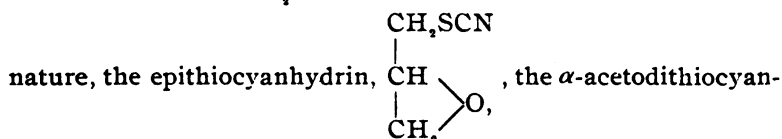
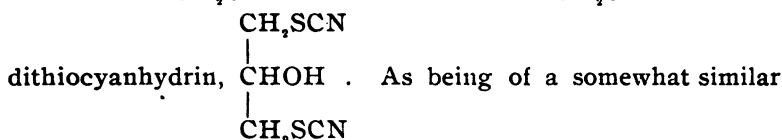
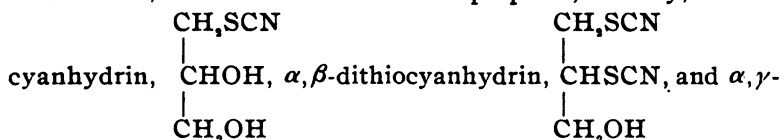
Received July 7, 1898.

THE alcohols form the most important class of organic compounds which have no representatives containing the thiocyan group. It would seem that such compounds would be produced by the double decomposition between alcohols having one or more atoms of hydrogen displaced by halogen and a metallic thiocyanate, and it was with this expectation that the following experiments were undertaken. In all cases tried, a reaction occurred as was shown by the separation of the halogen

<sup>1</sup> Read at the meeting of the New York Section, May 6, 1898.

salt. The thiocyanates formed, however, seem to be very unstable, easily changing to resinous substances, and much difficulty was experienced in separating and purifying them. In some cases it was found impossible.

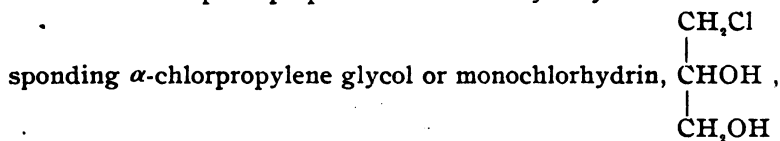
The particular thiocyan alcohols, whose preparation was undertaken, are those derived from propane; namely,  $\alpha$ -thio-



were prepared.

#### $\alpha$ -THIOCYANHYDRIN.

For the attempted preparation of  $\alpha$ -thiocyanhydrin the corre-



was used.

A mixture of fourteen grams of monochlorhydrin and thirteen grams of potassium thiocyanate, with ninety-five per cent. alcohol for solution, were heated on the water-bath with a return condenser. A crystalline precipitate of potassium chloride gradually formed. After four days of heating, four grams of potassium chloride in place of ten grams, theoretical quantity,

had separated. The filtrate from the potassium chloride was again heated. Only a little more of the chloride separated but there formed a considerable amount of a white resinous substance, some of which was removed from the flask and examined. Washed with hot water and alcohol it is a white or light yellow, brittle, odorless substance. It is insoluble in ordinary organic solvents, including water, alcohol, ether, benzene, chloroform, carbon disulphide, benzine, kerosene, gasolene, and toluene. It is unaffected by hydrochloric, acetic, and sulphuric acids or by ammonium hydroxide or strong aqueous potassium hydroxide. Bromine decomposes it with the production of a tar-like substance. Strong nitric acid oxidizes it, producing sulphuric and oxalic acids. This is an interesting reaction since it shows that the sulphur is much less closely bound to the radical than in the case of thiocyanates, mercaptans, and sulphides which, by oxidation with nitric acid, yield sulphonic acid, sulphoxids, and similar compounds.

That this resinous substance is not a thiocyanate is shown by the following facts: It does not give a sulphide with potassium hydroxide. It does not give a mercaptan with zinc and sulphuric acid. It does not give a sulphide and potassium thiocyanate with potassium sulphide. It does not give a sulphonic acid by the oxidation with nitric acid. Its solubilities are not those of known thiocyanates.

An analysis of the substance carefully washed with water and alcohol and dried to a constant weight, gave the following percentages, from which it is impossible to calculate any simple formula:

	I.	II.	III.	IV.	V.	Average.
Carbon .....	40.127	40.163	....	....	....	40.145
Hydrogen .....	5.185	5.15	....	....	....	5.168
Nitrogen .....	....	....	7.531	7.590	....	7.560
Sulphur .....	....	....	....	....	27.281	27.281
Oxygen .....	....	....	....	....	....	19.846

These percentages indicate that a secondary reaction has produced a complex condensation product. The absence of any solvent prevented any attempt to crystallize this compound. A flask, containing a mixture of potassium thiocyanate and monochlorhydrin, after heating was set aside. After several weeks it



was examined and well-formed crystals were found. The properties of these crystals were identical with those of the substance just described.

Besides the insoluble white substance there was also found, in the alcoholic filtrate from the potassium thiocyanate and monochlorhydrin, a very small amount of oil having the garlic odor characteristic of the organic thiocyanates. This oily liquid is extremely unstable. Any attempt to purify it changes it to the insoluble white substance. Apparently the monothiocyanate is first formed by the reaction, and by some secondary condensation the insoluble compound results.

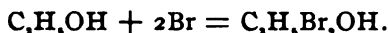
The reaction between potassium thiocyanate and monochlorhydrin was also tried at higher temperatures. Sealed tubes containing these two compounds in the ratio of their molecular weights, with alcohol as a solvent, were heated to different temperatures. Below  $100^{\circ}$  the action was very slow. From  $110^{\circ}$  to  $115^{\circ}$  the reaction was complete in six hours. At  $120^{\circ}$  and above there was much decomposition. In all cases the products are the same: the insoluble white compound and a trace of what was considered the monothiocyanhydrin. It was impossible to secure this in amount sufficient for further study.

$\alpha,\beta$ -DITHIOCYANHYDRIN.

$$\begin{array}{c} \text{CH}_2\text{Br} \\ | \\ \text{The } \alpha,\beta\text{-dibromhydrin, } \text{CHBr} \\ | \\ \text{CH}_2\text{OH} \end{array}$$

, to be used in the prepara-

tion of  $\alpha,\beta$ -dithiocyanhydrin, was obtained by the direct addition of bromine to allyl alcohol,

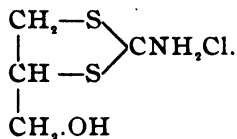


The product was purified by distillation *in vacuo*.

An alcoholic solution of forty grams of this dibromhydrin and thirty-seven grams of potassium thiocyanate were heated on the water-bath for six days. Somewhat more than half the theoretical quantity of potassium bromide separated. As there were signs of decomposition the heating was stopped. By evaporation of the alcohol, washing with water, and collecting with ether, about ten cc. of a dark-colored liquid was obtained.

Heated with potassium sulphide solution it gave potassium thiocyanate easily identified by the ferric chloride test. On heating or attempting to distil with steam it was resinified.

The reaction was next tried in sealed tubes. The tubes were charged with potassium thiocyanate and dibromhydrin, in the ratio of two molecules of the former to one of the latter. Alcohol was added as a solvent. Between  $110^{\circ}$  and  $115^{\circ}$  the reaction was complete in about eight hours. At higher temperatures there was much decomposition. In all cases there was a tendency to produce an amorphous substance similar to that from the monochlorhydrin. The contents of the tube were treated with warm alcohol. The alcoholic solution filtered from the potassium bromide was slowly evaporated to a small bulk and carefully washed with water to remove any unchanged potassium thiocyanate. There was left an oily liquid which could be further purified by solution in ether. This treatment does not remove all the unchanged dibromhydrin. The compound decomposes on heating, hence cannot be distilled. The difficulty of securing a pure sample prevented analysis. That the liquid is dithiocyanhydrin is shown by the fact that it gives potassium thiocyanate on heating with potassium sulphide, and the yield of potassium bromide is nearly equal to the theoretical. Additional proof is found in the preparation from it of imino-methanepropylalcohol disulphide hydrochloride of the formula



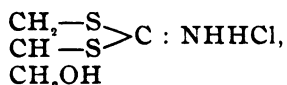
A similar reaction is found in the case of methylene dithiocyanate and propylene dithiocyanate. Both compounds have adjacent thiocyan groups as in the case of the compound under discussion and both give imino compounds similar to that above.<sup>1</sup>

About ten cc. of dithiocyanhydrin was poured into fifty cc. of water and a few grams of granulated tin added. The mixture was carefully heated on the water-bath and hydrochloric acid added. In the course of an hour's boiling the oily dithiocyan-

<sup>1</sup> Hagelberg: *Ber. d. chem. Ges.*, 23, 1083.

hydrin disappeared. Upon evaporation to a small bulk crystals appeared. When the liquid was left to spontaneous evaporation large octahedrons were obtained of iminomethanepropylalcohol disulphide tin hydrochloride.

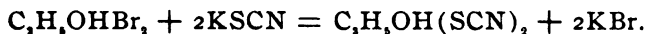
The compound is not stable in solution as the tin (stannous) is oxidized at the expense of the rest of the compound producing stannic chloride and a resinous substance. It was found advisable to precipitate the tin immediately after the dithiocyanhydrin had gone into solution, with hydrosulphuric acid, leaving the hydrochloric salt of iminomethanepropylalcohol disulphide in solution. The solution, filtered from the tin sulphide, was evaporated to dryness on the water-bath. The residue was dissolved in alcohol, filtered, evaporated to a small bulk, and allowed to crystallize. Transparent, colorless, well-formed, tetragonal crystals separated. A determination of the chlorine gave 20.21 per cent., while the formula



requires 20.08 per cent.

This iminomethanepropylalcohol disulphide hydrochloride is very easily soluble in water, somewhat soluble in alcohol, and insoluble in ether and chloroform.

The preparation of this compound taken with the reactions with potassium sulphide and the amount of potassium bromide separated, identify the dithiocyanhydrin. The reaction for its preparation is



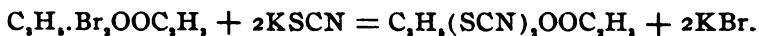
In its physical properties it closely resembles the propylene-dithiocyanate. Both are liquids of garlic-like odor, insoluble in water, but soluble in alcohol and ether. Both are decomposed by heat and resinified by acids and alkalies. By nitric acid both are oxidized, producing sulphuric acid and, in the case of dithiocyanhydrin, oxalic acid is also formed. The action of the nitric acid seems to be to first produce a substance similar to the amorphous compound from the monochlorhydrin which is then oxidized as above.

$\alpha$ -ACETODITHIOCYANHYDRIN.

Acetodibromhydrin, or dibrompropyl acetate, is prepared by the action of acetic anhydride on the  $\alpha,\beta$ -dibrompropyl alcohol.<sup>1</sup> It was washed with water and a dilute carbonate solution, dried and rectified under diminished pressure.

A sealed tube containing seventeen grams of acetodibromhydrin, thirteen grams of potassium thiocyanate, and ten cc. of alcohol, was kept at 120° for four hours. On opening, nearly the theoretical quantity of potassium bromide was found. The alcoholic filtrate from the potassium bromide was poured into water and about fifteen cc. of a heavy liquid, insoluble in the water, separated. This was washed several times with water to free it from traces of potassium bromide and thiocyanate. It was then dissolved in ether to free it from decomposition-products. On evaporation there was left a clear, red-colored liquid, giving with potassium sulphide, potassium thiocyanate. This compound, like the corresponding alcohol, cannot be distilled and is easily decomposed by most reagents. With tin and hydrochloric acid it gave reactions similar to those with the alcohol.

The compound was not analyzed but the reactions show it to be acetodithiocyanhydrin. The reaction is:

 $\alpha,\gamma$ -DITHIOCYANHYDRIN.

The dichlorisopropyl alcohol or dichlorhydrin was prepared by treating anhydrous glycerine with chloride of sulphur at 100°. The product was fractionally distilled and the fraction collected between 176° and 178° was used in these experiments.

A mixture of twelve and five-tenths grams of the dichlorhydrin and nineteen grams of potassium thiocyanate in alcoholic solution was heated on the water-bath for four days. About six grams of potassium chloride had separated, less than half the theoretical amount. The contents of the flask had the odor of the thiocyanates. In addition to the potassium chloride there had also separated a spongy mass, of a yellow color, and in appearance not unlike the insoluble compound obtained from the monochlorhydrin. On examination it showed the same properties. It was insoluble in the organic solvents. It was unaffected by acids or alkalis.

<sup>1</sup> Aschan: *Ber. d. chem. Ges.*, 23, 1827.

lies. Reducing agents do not change it; strong nitric acid oxidizes it to sulphuric and oxalic acids. It is apparently a condensation-product similar to that obtained in case of monochlorhydrin.

In the alcoholic filtrate from the above compound was found a very small amount of a liquid, insoluble in water, having the characteristic odor of the thiocyanates. It may have been either the dithiocyanhydrin sought or the chlorthiocyanhydrin. Its insolubility in water would distinguish it from the dichlorhydrin. It was unstable and attempts to purify it sufficiently to test resulted in its decomposition.

This reaction was also tried in sealed tubes. A tube, heated to 130° for six hours, contained much unchanged potassium thiocyanate. Considerable of the spongy substance was found and a trace of the oily compound mentioned above. A tube heated to 175° for two hours gave the best results. The action was nearly complete. Less of the amorphous substance was formed. At higher temperatures there was much decomposition and pressure produced. In all cases the same results were obtained. I was unable to separate and purify a compound containing the thiocyan group.

*β*-ACETO-*α,γ*-DITHIOCYANHYDRIN.

The corresponding acetic ester, the dichlorisopropylacetate, was also tried. The ester was prepared according to the method of Berthelot and Luca.<sup>1</sup> Anhydrous glycerine was treated with acetyl chloride and the product purified by fractional distillation.

A sealed tube containing dichlorpropyl acetate and potassium thiocyanate in the ratio of one molecule of the former to two of the latter, with alcohol for solution, was heated to 130° for six hours. The action was incomplete and the tube was heated to 180°. There was some decomposition. A large amount of amorphous substance resembling those already described was present. A small amount of oil was also found as in the case of the corresponding alcohol. Here, again, apparently the thiocyanate is formed but suffers secondary decomposition resulting in the insoluble amorphous substance.

<sup>1</sup> *Ann. chim. phys.* [3], 52, 459.

## EPITHIOCYANHYDRIN.

Epithiocyanhydrin proved much easier in preparation and more interesting in reactions. For its preparation both epichlor-

hydrin,  $\begin{array}{c} \text{CH}_2\text{Cl} \\ | \\ \text{CH} \\ | \\ \text{CH}_2 \end{array} > \text{O}$ , and epibromhydrin were used. Epichlorhy-

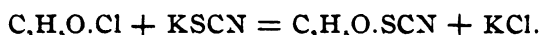
drin was obtained by the action of a strong aqueous solution of potassium hydroxide on dichlorisopropyl alcohol. The epibromhydrin was obtained in a similar manner from  $\alpha,\beta$ -dibrompropyl alcohol. Both compounds were purified by distillation.

There is no reaction between epibrom- or epichlorhydrin and potassium thiocyanate at ordinary temperatures. Mixtures of these substances have stood for several days without reaction. At  $40^\circ$  to  $50^\circ$ , however, the action goes on nicely. The theoretical amount of potassium halogen salt is separated in a few hours. At higher temperatures the action is violent; at  $100^\circ$  it is very rapid and there is much decomposition. The purification of the epithiocyanate is somewhat difficult as heat decomposes it. The alcoholic solution, filtered from the separated potassium chloride or bromide is evaporated to a small bulk, keeping the temperature below  $50^\circ$ . Water is then added to wash out the excess of potassium thiocyanate. A thick insoluble liquid separates; this is the epithiocyanhydrin holding in solution much decomposition matter. It can be freed from this, after washing with water, by solution in ether. The evaporation of the ether leaves the epithiocyanhydrin as a clear liquid of a dark red color, and having a disagreeable garlic odor. It is insoluble in water but soluble in alcohol, ether, and chloroform. It cannot be distilled. On the skin it produces a burning or smarting sensation. With potassium sulphide it gives potassium thiocyanate. With nitric acid it behaves like the compounds already described: the acid first resinifies and then oxidizes to sulphuric and oxalic acids.

A determination of the nitrogen confirms the qualitative results:

	Per cent.
Nitrogen found .....	11.914
Necessary for formula, $\begin{matrix} \text{CH}_2\text{SCN} \\ \text{CH} \\ \text{CH}_2 > \text{O} \end{matrix}$ .....	12.17

The reaction is :



#### ACTION OF HYDROSULPHURIC ACID ON EPITHIOCYANHYDRIN.

Dry hydrosulphuric acid has an interesting reaction on the thiocyanates of the marsh-gas series. It forms the esters of dithiocarbamic acid which are readily crystallizable. About ten cc. of epithiocyanhydrin was treated with hydrogen sulphide under a pressure of one atmosphere and eight inches of mercury. The experiment was tried both at ordinary temperatures and at  $100^\circ$ . In both cases the result was the same. No carbamic ester was formed, but thick sirupy liquid of a very disagreeable odor, insoluble in water and sparingly soluble in alcohol, carbon disulphide, and chloroform. Its alcoholic solution was precipitated by soluble lead, mercury, silver, and copper salts, but was unaffected by mercuric or lead oxids. These reactions indicate the formation of a sulphide.

#### EPIHYDRINDIMETHYLSULPHIN IODIDE.

A reaction similar to that used by Cahours in the preparation of trimethylsulphin iodide was tried. About five cc. of epithiocyanhydrin with fifteen cc. of methyl iodide (an excess) were sealed in a tube and kept at  $100^\circ$  for six hours. On examination crystals were found in the tube. A similar mixture was allowed to stand for several days at the ordinary temperature, and crystals also separated in this case. The crystals were clear, colorless, monoclinic plates. They were purified by recrystallizing from water and washing with alcohol. They gave good qualitative tests for both sulphur and iodine. The iodine was determined both by titration, with a standard silver nitrate solution, and by weighing the precipitated silver iodide :

	Per cent.
Iodine found .....	51.392
Necessary for the formula, $\begin{matrix} \text{CH}_2(\text{CH}_3)_2\text{SI} \\ \text{CH} > \text{O} \\ \text{CH}_2 \end{matrix}$ .....	51.430

The crystals decompose without melting between  $195^{\circ}$  to  $200^{\circ}$ .

The small amount of material prevented farther experiments.

The compounds most closely related to epithiocyanhydrin are the thiocyanacetone and thiocyanpropyl aldehyde. It resembles both in physical properties and in its unstable character.

The thiocyanacetone was reported by Tscherniac in 1883. It is an oil of very disagreeable odor and easily decomposed by heat.

The  $\beta$ -thiocyanpropyl aldehyde was prepared by Chautard.<sup>2</sup> It is a liquid of fetid odor, is decomposed by heat, and is easily resinified by acids and alkalis.

#### CONCLUSION.

The results of the experiments may be summarized as follows :

The monochlorhydrin, the  $\alpha,\gamma$ -dichlorhydrin, and the acetodichlorhydrin, form corresponding thiocyanates which are very unstable and immediately change to complex secondary compounds.

The  $\alpha,\beta$ -dibromhydrin and its acetic ester form dithiocyanates which are somewhat more stable and can be separated and purified. Treated with tin and hydrochloric acid they give double chlorides of tin and iminomethanepropylalcohol disulphide.

The epichlorhydrin forms the epithiocyanhydrin readily. It is a liquid of garlic odor, insoluble in water, but soluble in alcohol and ether. It cannot be distilled. With dry hydrosulphuric acid it forms epihydrin sulphide rather than a dithiocarbamic ester. With methyl iodide it forms epihydrindimethylsulphine iodide.

ORGANIC LABORATORY, HAVEMEYER HALL,  
COLUMBIA UNIVERSITY.

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### LUBRICANTS FOR GLASS STOP-COCKS.

BY FRANCIS C. PHILLIPS.

Received July 18, 1898.

THE success of modern chemical research work depends frequently upon the maintenance in position for considerable periods of complex forms of apparatus in which glass stop-

<sup>1</sup> Tscherniac: *Ber. d. chem. Ges.*, 16, 349.

<sup>2</sup> Chautard: *Ann. chim. phys.* [6], 16, 197.



cocks play an important part, and the failure or breakage of a stop-cock often proves to be the cause of serious loss of time or material. The efficiency of a stop-cock is, however, quite as much dependent upon the lubricant used for its protection as upon the skilful workmanship of the glass-blower in its manufacture.

It has been the common practice to employ an animal fat or a mixture of such fats for lubricating the stop-cock plugs of apparatus of all kinds and for work of every description, although it is a fact of experience that such lubricants are often a source of inconvenience and even danger to the apparatus.

A stop-cock lubricant should, besides overcoming friction, satisfy the following requirements:

1. It should adhere to the glass and should not be loosened by water.
2. It should be little affected by changes of temperature.
3. It should not be saponified by alkali.
4. It should be sufficiently transparent or translucent to render visible any clogging of the hole in the stop-cock plug while in use, and to show whether air spaces occur between the plug and the walls of the stop-cock.

Ordinary fats are so easily saponified and adhere so feebly to glass that they are seldom suited to the purpose. Pure rubber heated to a temperature sufficient to render it permanently viscid, has advantages over fats, but its adhesiveness is lessened by moisture, and it is completely removed by alkali.

Schmitz<sup>1</sup> recommends for glass stop-cocks the use of gutta percha dissolved in a high-boiling mineral oil. This mixture, although not saponifiable, does not adhere well to glass. If thinned down sufficiently with oil, its lubricating qualities suffer, while the gutta percha tends to become granular if the mixture is made thicker.

Vaseline, which is sometimes recommended for use alone, does not adhere to the glass, and does not overcome friction.

With a view to producing a lubricant better adapted to use on glass stop-cocks, a series of experiments has been tried. Various mixtures of softened rubber with other substances were tested. On mixing together

<sup>1</sup> *Ztschr. anal. Chem.*, 1884, 516.

	Parts.
Pure rubber.....	70
Spermaceti.....	25
Vaseline. ....	5

a mass is obtained which lubricates well, is translucent, adheres to the glass, and is not saponifiable. The vaseline was added to the mixture to increase its softness. The materials were thoroughly mixed while hot, the rubber being melted first, and the others stirred in. It is well to use a little more vaseline in winter than summer.

Another preparation, which gave still better results, was made by mixing

	Parts.
Pure rubber.....	70
Yellow unbleached beeswax .....	30

The rubber should be pure and fresh. Old rubber, or scraps of worn-out tubing, whether black or red, will not answer as well and may cause the mixture to become more or less granular and opaque when used in the stop-cocks. The rubber is best heated in a covered vessel until thoroughly melted, and then the wax should be added. The hot mixture is well stirred. No vaseline is needed. This lubricant is very serviceable, protects stop-cocks from sticking, even when used for concentrated solutions of caustic alkalies, and is quite translucent in thin layers. Care should be used not to scorch the mixture in its preparation. Strong alkalies tend in time to loosen and emulsify all lubricants and the stop-cocks should occasionally be cleaned and recoated.

It has been attempted to increase the adhesiveness of such lubricants by the addition of small quantities of balsam of fir and other strongly adhesive substances, but difficulty was found from the tendency to cause sticking of the stop-cock plug. The rubber mixtures should not be exposed to the air longer than is necessary during the heating, and they should be preserved in closed bottles.

Various mixtures of gutta percha with wax and with oils were tried but the gutta percha tends to cause granulation and diminishes adhesiveness. The mixtures above recommended may be readily removed from parts of glass apparatus which are difficult of access for cleaning, by the use of a little concentrated

nitric acid, which quickly attacks and loosens it so that it may be washed out by water.

No lubricant is fit for use unless it renders the stop-cock nearly or quite translucent, so as to show whether or not the plug is coated over its entire length.

A thick rubber and wax mixture is especially suited for well-ground glass stop-cocks upon gas vessels which are to be exhausted and which have therefore to sustain the full pressure of the atmosphere. Such mixtures have been in use for stop-cocks of ordinary burettes in volumetric work during about two years and have given satisfactory results in every way.

WESTERN UNIVERSITY LABORATORY,  
ALLEGHENY, PENNA.

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**ABSTRACT OF A DESCRIPTION OF A RESPIRATION CALORIMETER FURNISHED BY PROFESSORS  
ATWATER AND ROSA.<sup>1</sup>**

BY C. F. LANGWORTHY.

Received August 6, 1898.

**I**N 1892 Professors Atwater and Rosa undertook the development of an apparatus for measuring the income and outgo of matter in the animal body. It was proposed, among other things, to study the application of the law of conservation of energy in the animal organism, and plans were made for experiments with man. These required a respiration calorimeter large enough to accommodate a man in comparative comfort for several days at a time and capable of measuring accurately the total income and outgo of matter and energy. The work has been carried out at Wesleyan University, Middletown, Conn., where the facilities of the chemical and physical departments and the mechanical laboratory were made available. The work has been conducted with funds and appliances supplied by the U. S. Department of Agriculture, the Storrs Connecticut Experiment Station, and Wesleyan University.

Considerable time was spent in elaborating the apparatus until it was sufficiently perfected for use in experiments with man. That part which has to do with measuring the income and outgo of matter is similar in principle to the respiration apparatus of

<sup>1</sup> Read at the Sixteenth General Meeting of the American Chemical Society at Washington, D. C., December, 1897.

Pettenkofer and Voit. Many improvements and additions have, however, been made. The appliances for measurement of heat are entirely original. Advantage has been taken of recent progress in electrical science and other branches of physics, and the result is an instrument of remarkable accuracy, notwithstanding its large size.

The portion of the apparatus which has to do especially with respiration experiments has been described in detail in Bulletin No. 44 of the Office of Experiment Stations of the U. S. Department of Agriculture, and the results of four experiments, which include the balance of income and outgo of nitrogen and carbon, are reported in detail. In one of these experiments the subject remained in the respiration chamber for twelve days.

At the meeting of the British Association for the Advancement of Science at Toronto, in 1897, Professor Rosa read a paper describing at some length the special devices used in the measurement of heat and energy produced by the subject in the calorimeter. Brief reference will be made here only to the principal points.

The respiration calorimeter is situated in the basement of the Orange Judd Hall of Natural Science at Wesleyan University.

The respiration chamber is a room or box in which a man may live comfortably during the period of an experiment. The inside dimensions are: Length, 2.15 meters; width, 1.22 meters; height, 1.92 meters. It is provided with conveniences for sitting, sleeping, eating, and working, as well as arrangements for ventilation and for the study of the respiratory products. The chamber consists, in fact, of three concentric boxes, the inner one of metal and the two outer ones of wood. The inner box, of which the inside dimensions have just been given, is double-walled, the inner wall being of sheet copper, the outer of sheet zinc. The two walls are eight cm. apart. This double-walled box is held in shape by a wooden framework between the two metal walls. The inside volume is approximately four and eight-tenths cubic meters.

The limits of this abstract prevent any extended description of the devices used for measuring the incoming and outgoing currents of air or those for measuring the heat produced inside the respiration chamber. A number of improvements suggested

by observation and experiment have been made. For instance, the air as it enters and leaves the chamber is practically freed from moisture by freezing. This greatly facilitates its analysis. The amount of water removed can be accurately determined by weighing.

Since the experiments reported in Bulletin No. 44 were made, meter pumps have been built by the University mechanician, Mr. Blakesley, which render the measurement of the air more simple and accurate. The length of stroke and the volume of air per stroke can be determined, and thus the volume of air drawn through the apparatus may be measured. The pumps are also arranged to deliver an aliquot part of the air for analysis.

In the experiments with man the food, urine, and feces were analyzed by the official methods and the heats of combustion were determined by the bomb calorimeter. No balance of income and outgo of energy was reported in Bulletin No. 44. A considerable number of experiments with man have been made since the publication of that bulletin in which the balance of income and outgo of heat was determined.

The calorimeter is so arranged that the inner and outer metal walls may be kept at the same temperature. When this is done no heat will pass from the inside out or the outside in. The temperature of the inner and outer walls is measured by special devices and the air spaces adjoining the metal walls may be heated or cooled as is shown to be necessary. Since no heat can be lost by passing through the walls of the chamber it only remains to measure the heat generated in it. The means employed are the reverse of those used in heating buildings with hot water. That is, the heat is absorbed by a current of cold water passing through radiators or absorbers. The temperature of the incoming and outgoing currents of water is very carefully determined, and knowing this and the volume of water passing through the absorbers in a given time, the amount of heat produced can be calculated. The current of air necessary for ventilation is kept at the same temperature as it enters and leaves the chamber, hence no heat escapes except by the stream of water and by the latent heat of water vapor passing out with the ventilating current of air.

A number of electrical tests were made of the accuracy of the calorimeter as regards measurement of heat. For this purpose a wire resistance coil was placed inside the chamber. This was connected with wires passing through the wall to the outside and connected with a voltmeter and an ammeter and, in some instances, a Thompson balance. The amount of heat given off inside the apparatus was calculated from the current and was also determined in the water passing through the absorbers. The details of the arrangements and observations are reserved for future publication by the investigator. The results are given in Table I :

TABLE I.  
SUMMARY OF ELECTRICAL TEST EXPERIMENTS.

Date.	Duration. Hours and minutes.	Heat as measured.	Capacity correction.	Corrected heat.	Theo- retical heat.	Per cent. measured.
	H. M.	Cal.	Cal.	Cal.	Cal.	
March 20, 1897..	13 20	1001.9	—9.0	992.9	989.5	100.3
March 25, 1897..	6 05	528.8	—6.0	522.8	522.1	100.1
March 26, 1897..	7 17	1252.1	—1.2	1250.9	1253.1	99.8
April 30, 1897...	6 00	21.4	0.0	21.4	21.5	99.5
	....	....	....	2788.0	2786.2	100.1

One objection to this use of the electrical method as a test of the accuracy of the apparatus is found in the fact that the conditions were not the same as obtained in an experiment with a man. There was no ventilating current of air through the apparatus, and no water or carbonic acid was given off within it. A number of check experiments were therefore made with ethyl alcohol, and a current of air was passed through the apparatus as in experiments with man. The heat of combustion of the ethyl alcohol was determined by burning it in the bomb calorimeter. These check experiments were made before and after each experiment with a man. In every case the alcohol was burned for a time, generally from three to six hours, before the experiment proper began, the object being to get the temperature of the interior of the apparatus, the moisture content of the air, and the moisture adhering to the inner walls and the heat absorbers as nearly as possible in equilibrium. The attempt was made to have the temperature and moisture content of the air during the last three to six hours of the experiment

the same as in this preliminary period, on the assumption that under these conditions the amounts of moisture in the apparatus would be the same at both times. The quantities of water and carbon dioxide in the air at the beginning and at the end of the experiment were determined in samples of about ten liters drawn out for the purpose.

The apparatus and the conditions of the experiment were such as to permit reasonable uniformity in the flow of the ventilating current of air through the chamber, the rate of combustion of alcohol, the consequent production of carbon dioxide, water vapor, and heat, and the temperature of the interior of the chamber. From 500 to 1,000 cc. of ethyl alcohol was burned in the respiration chamber and the carbon dioxide, water, and heat produced were measured. The results are briefly summarized in Table II.

Considered as results of analyses and of determinations of the heat of combustion of ethyl alcohol, these figures for experiments 1, 2, and 4 would compare with the theoretical figures as shown in Table III.

*Note.*—Since the above abstract was prepared, a number of additional check experiments with alcohol have been made with the respiration calorimeter, as well as experiments with man, in which the income and outgo of energy was determined, in addition to the balance of income and outgo of carbon and nitrogen. The check experiments and two experiments with man have been reported by Professors Atwater and Rosa in the Tenth Annual Report of the Storrs Connecticut Experiment Station (pages 212-242). The results of the alcohol check experiments are shown in Table IV.

In one experiment with a man the energy of the material actually oxidized in the body was calculated to be 3,864 calories per day. The heat measured by the calorimeter was 3739 calories. In the other experiment with a man the energy of the total material oxidized in the body was 2354 calories per day. The heat measured by the calorimeter was 2329 calories. In other experiments not yet reported the measurements agreed with the theoretical values within one per cent. or less.

The results obtained in the check experiments and in experiments with man are extremely accurate. It would appear that

TABLE II.—SUMMARY OF RESULTS OF ALCOHOL CHECK EXPERIMENTS.

No. of experiment.	Date, 1897.	Duration, Hours and minutes.	Alcohol burned.		Carbon dioxide.		Water.		Heat.	
			Grams.	H. M.	Required.	Found.	Required.	Found.	Required.	Found.
1	April 27-29	52 30	955.4		1,659.0	1,657.7	1,106.4	1,109.6	5,449.9	5,380.1
2	May 10-11	29 56	798.8		1,387.5	1,385.5	924.8	925.6	4,556.6	4,538.8
3	May 26-27	33 50	505.4		877.6	882.9	585.3	649.7 <sup>1</sup>	2,882.9 <sup>1</sup>	2,868.5
4	November 2-3	35 9	788.2		1,366.6	1,374.6	912.4	920.9	4,488.1	4,478.8

TABLE III.

DETERMINATIONS OF RESPIRATION CALORIMETER COMPARED WITH THEORETICAL FIGURES FOR CARBON AND HYDROGEN AND HEAT OF COMBUSTION OF ALCOHOL.

	Experiment 1.		Experiment 2.		Experiment 4.		Average.		Theoretical.	
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Carbon .....	52.12	52.12	52.54	52.16	52.10	52.17	52.26	52.17	52.17	52.17
Hydrogen .....	13.08	13.05	13.16	13.16	13.10	13.04	13.10	13.04	13.04	13.04
Heat of combustion .....	98.70	100.00	99.80	99.80	99.50	100.00	99.50	100.00	100.00	100.00

TABLE IV.—RESULTS OF ALCOHOL CHECK EXPERIMENTS.

Date.	Duration, Hours and minutes.	Alcohol burned.		Carbon dioxide.		Water.		Heat.	
		Grams.	H. M.	Theoretical.	Found.	Theoretical.	Found.	Calculated.	Found.
1898.									
January 6 .....	5 50	112.2		193.7	193.3	129.8	131.3	635.6	647.3
January 24-27 .....	83 44	1607.8		2787.0	2771.0	1861.3	1884.5	9153.2	9127.7
May 9-10 .....	24 00	503.9		867.9	863.7	586.6	584.8	2874.3	2862.0
Total .....	113 34	2223.9		3848.6	3828.0	2577.7	2600.6	12663.1	12637.0
									99.8

<sup>1</sup> The excess of water and deficiency of heat are assumed to be due to evaporation of water inside the chamber.



the discrepancies are well within the limits of experimental error. In other words, the respiration calorimeter, although complicated and of such size and construction that a man may remain in it with comfort for a number of days or weeks, will measure carbon dioxide, water, and heat given off in the respiration chamber as accurately as these factors are measured by the usual laboratory methods. The accuracy obtained is much greater than with any similar apparatus with which we are familiar.

Improvements in details are constantly being made. In general, it may be fairly said that the object sought has been accomplished; that is, that the balance of income and outgo of matter and energy of the human subject may be accurately measured during comparatively long periods of time.

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[CONTRIBUTION FROM THE LABORATORY OF ANALYTICAL CHEMISTRY,  
UNIVERSITY OF MICHIGAN.]

## ELECTROLYTIC DETERMINATION OF TIN IN TIN ORES.

BY E. D. CAMPBELL AND E. C. CHAMPION.

Received August 8, 1926.

**I**N the methods at present in use for the determination of tin in tin ores, the decomposition is effected by fusion with sodium carbonate and sulphur, in order to form sodium sulphostannate, from which the tin is obtained either by precipitation as sulphide with subsequent ignition to the oxide or by electrolytic deposition from the ammonium sulphide or oxalate solution. Some of the objections to the Rose method of precipitation as stannic sulphide and subsequent weighing as stannic oxide are the difficulties of washing the sulphide free from sodium salts, the ignition to stannic oxide without loss of stannic sulphide, and the contamination of stannic oxide with silica.

Electrolytic deposition of tin from the ammonium sulphide solution does not seem to give entirely satisfactory results, for although the tin may be completely precipitated, it is very difficult to obtain complete deposition without at the same time precipitating some sulphur. On the other hand, under proper conditions tin may be very satisfactorily deposited electrolytically from the double oxalate solution; and in the method herewith proposed the principal modification is in the method of convert-

ing the tin from the sulphostannate into the double oxalate. In the method as given by Classen for the conversion of sodium sulphostannate into the double ammonium oxalate, the solution of the sulphostannate is first acidified with sulphuric acid and the tin then oxidized to metastannic acid by means of hydrogen peroxide. The metastannic acid so formed has to be filtered, washed, and dissolved by means of ammonium acid oxalate and oxalic acid, in order to convert it into the double oxalate ready for electrolysis. It was in order to avoid any necessity of precipitating the tin and filtering it out, after it had been once obtained in solution as sodium sulphostannate, that the method given below was perfected. The method in detail, which has given us very satisfactory results on ores tested, is as follows :

Mix one gram of finely ground ore intimately with five to six grams of a fusing mixture made up of equal weights of dry sodium carbonate and sulphur. Place the ore so mixed in a covered porcelain crucible which in turn should be in a larger covered porcelain crucible. This arrangement of double crucibles will prevent oxidation of stannic sulphide during the ignition. Place the crucible upon a triangle and cover with a large Hessian or clay crucible, from which the bottom has been removed, in such a way that the heat from the burner used in the ignition will be kept in, so that the whole of the porcelain crucible will be evenly heated. Raise the temperature of the porcelain crucibles by means of a good burner, such as the Detroit or Fletcher style, to a full red heat, and maintain the temperature for one hour. After allowing it to cool, place the inner crucible in a beaker or casserole and dissolve out the sodium sulphostannate by heating with forty or fifty cc. of water. After complete disintegration of the fused mass, remove the porcelain crucible from the solution and filter out the insoluble oxides and sulphides from the solution, which will contain almost all the tin as sodium sulphostannate. Wash the insoluble residue with hot water. This insoluble residue will usually carry a small amount of tin and must therefore be ignited in the crucible, in which the fusion was performed and after ignition be re-fused as in the first case, with fresh sodium carbonate and sulphur. After fusing the insoluble residue from the first fusion and dissolving out the tin, unite the solutions of sodium sulpho-

stannate. Add to the united solutions of sodium sulphostannate hydrochloric acid, until the solution is slightly acid and the tin has been precipitated as stannic sulphide. Boil down rapidly, until the excess of hydrogen sulphide has been boiled off and the bulk of the solution has been reduced to seventy-five or eighty cc. Add to the hot solution ten cc. of hydrochloric acid (sp. gr. 1.20). Then stir in, a little at a time, sodium peroxide, until the stannic sulphide has been completely oxidized to stannic chloride and the solution has become clear, except for a little sulphur which collects easily on boiling for two or three minutes and can be easily removed by filtering.

The oxidation of stannic sulphide to stannic chloride is very easily effected, requiring usually from two to three grams of sodium peroxide. After oxidizing the stannic sulphide to stannic chloride, boil two or three minutes until the separated sulphur is collected, then filter into a large platinum dish, and wash thoroughly with a little hot water. Add to the solution ammonia until a slight permanent precipitate is obtained, then fifty cc. of a ten per cent. solution of acid ammonium oxalate. This will give a clear solution from which the tin is easily deposited.

Electrolyze over night with a current  $N. D_{100} = 0.10$  ampere with an electromotive force of four volts. This current can be obtained from two storage cells using suitable resistance. In the morning the tin will be found to be completely precipitated as a pure white, firmly adherent metal upon the platinum dish. When eight volts E. M. F. were used the deposit was found to be more strongly crystalline and less firmly adherent than when lower voltage was employed. When the tin is completely deposited, disconnect and wash the tin first with water, then with alcohol. Drain off the latter as completely as possible and dry between  $80^{\circ}$  and  $90^{\circ}$  C. If the deposited tin is found to have small crystals of ammonium oxalate adhering to it, they may be easily removed by washing with a little warm water before the final washing with alcohol. After weighing the platinum dish containing the precipitated tin, the latter is dissolved off by heating with a little hydrochloric acid and the weight of the platinum dish obtained after washing and drying as before.

In electrolytic determination of metal where they are deposited in platinum dishes, the results will be found to be much more satisfactory, if duplicate determinations are made in platinum dishes of practically the same size, and the dishes are washed, dried, cooled, and weighed under the same conditions, each dish serving as a counterpoise for the other. By using dishes in this way, variations of weight due to atmospheric changes may be reduced to a minimum and the results made more accurate than when a dish is weighed alone.

ANN ARBOR, MICH., June 21, 1898.

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[CONTRIBUTIONS FROM THE LABORATORY OF ANALYTICAL CHEMISTRY,  
UNIVERSITY OF MICHIGAN.]

## ON THE INFLUENCE OF SILICON UPON THE HEAT OF SOLUTION OF COKE CAST IRONS.

BY E. D. CAMPBELL AND WM. E. HARTMAN.

Received August 8, 1898.

THE principal object of the following research was to determine if any thermochemical evidence could be obtained indicating a change in the condition in which silicon exists in cast iron, this change being due to differences of the temperature at which the iron is made. It is well known that when the temperature in a blast-furnace passes a certain point, namely, that at which No. 1 foundry iron is made, the color of the cast iron produced changes somewhat as the temperature of the furnace rises. This change continues until it reaches the temperature at which silvery or glazed iron is made, when there is a very abrupt change in the appearance and properties of the iron. It was thought that the appearance peculiar to silvery iron might be due to a change of form in which the silicon exists, and that this change might be indicated thermochemically.

The cast irons used in this work, with the exception of the two ferrosilicons, were all made in the same blast-furnace from approximately the same stock. They were selected from among a large number of samples with a view to obtaining a regularly increasing per cent. of silicon as the temperature at which the iron was produced increased, this temperature being judged by the grade of the iron.

The chemical analyses upon these irons included the deter-

minations of graphitic carbon, manganese, phosphorus, silicon, and total iron. In addition, after the samples had been dissolved in the calorimeter, the amounts of iron and phosphorus in the insoluble residue were determined. From these two latter results the amount of iron oxidized to ferrous chloride and of phosphorus oxidized to phosphoric acid could be found. All the manganese passes into solution as manganous chloride.

In the calorimetric determinations, a one-gram sample was used in all cases. The solvent was a solution of ammonium copper chloride made up in the molecular ratio,



but with the addition of 0.84 per cent. of free hydrochloric acid. It was found that when a sample of pure carbide of iron, of the empirical formula  $\text{CFe}_3$ ,<sup>1</sup> was treated with strictly neutral ammonium copper chloride solution, there was apparently no action at all, the carbide remaining unaltered. The addition of only 0.09 per cent. free hydrochloric acid induced marked action, while with 0.84 per cent. of free acid solution of one gram was complete in two minutes. Pure water acidified with 0.84 per cent. of free acid was without appreciable action upon the pure carbide of iron. Owing to the greatly increased chemical activity of a slightly acid solution, compared with that of a strictly neutral one, it was thought best to use the former, as there seemed to be no danger of direct reaction between the hydrochloric acid and the metal under treatment.

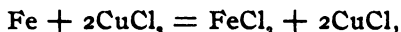
The rise of temperature of the solution in the calorimeter was determined by means of a Beckmann thermometer, graduated in hundredths of a degree, the graduations being large enough so that with the aid of a reading glass, readings could be made in thousandths of a degree, with an error not exceeding two thousandths. The rise of temperature in the calorimeter varied for the different samples between  $2.780^\circ$  and  $3.715^\circ$ .

Owing to the varying lengths of time required for solution of the different samples, corrections were made in all cases for the loss by radiation. In each calorimetric determination readings were made at the end of each minute until a fall in the thermometer indicated complete solution; and corrections were

<sup>1</sup> "A Pure Carbide of Iron"—*Am. Chem. J.*, 18, 836.

made for loss according to the difference in temperature at the time of each reading. The rate of loss by radiation for varying temperatures was determined for differences of  $1^{\circ}$ ,  $2^{\circ}$ , and  $3^{\circ}$  between the initial and final temperatures; and it was found that for twenty-five minutes, the rate of loss by radiation for any given difference, was constant. For a difference of  $3^{\circ}$  between the initial and final temperatures the rate of loss was  $0.015^{\circ}$  per minute. The correction that had to be applied because of this loss varied between 9.6 and 20.1 calories with the exception of one case in which the solution required twenty-two minutes, necessitating a correction of ninety-eight calories. It was also found that a second correction had to be made owing to the slow oxidation of the cuprous to cupric chloride by the air dissolved in the solution. This oxidation takes place most rapidly during the first ten minutes, after which the rate falls off as the amount of dissolved air present, diminishes. The correction due to this oxidation amounts to six-tenths of a calorie per minute for the first ten minutes, which amount falls to 0.36 calorie during the succeeding five minutes, and to 0.24 calorie at the end of fifteen minutes from the start. This correction was determined by dissolving 1.132 grams of pure copper, the chemical equivalent of one gram of pure iron, and noting the slow, continuous rise of temperature after the copper was completely in solution as cuprous chloride.

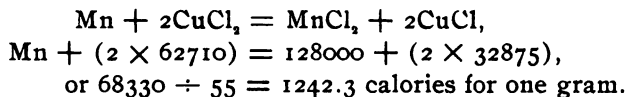
In the reduction of the results to absolute calories, since we had not access to apparatus for determining accurately the specific heat of a solution, resort was made to an indirect method for the determination of the water equivalent of our solvent. The following data were used: specific heat of glass, 0.177; specific heat of mercury, 0.033; specific heat of iron, 0.111; calories evolved by one gram of iron when dissolved in ammonium copper chloride, 719.3. This last figure was obtained from the heats of formation of ferrous, cupric, and cuprous chlorides as given in Thomsen's "Thermochemische Untersuchungen," 3, 506.



$$\begin{aligned} \text{Fe} + (2 \times 62710) &= 99950 + (2 \times 32875), \\ \text{or } 40280 \div 56 &= 719.3 \text{ calories.} \end{aligned}$$

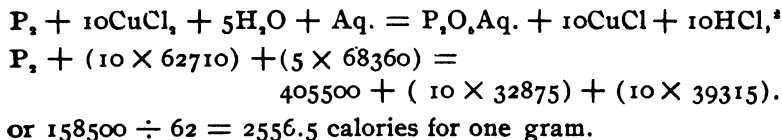
Figuring from these data, by dissolving one gram of pure iron and dividing 719.3 by the rise of temperature, correcting for loss by radiation and for gain by oxidation of cuprous chloride, the water equivalent of the solution used and containing vessel, thermometer, and stirrer could be calculated. By subtracting the water equivalent of these latter, the specific heat of the solvent was found. This gave 0.8226 as the specific heat of the solution used.

Since the cast irons, with the exception of the ferrosilicons which were nearly free from manganese, contained from 0.46 to 1.05 per cent. of manganese, a correction had to be made for the heat evolved in its solution. From the equation:<sup>1</sup>



This would require a correction of 1.24 calories for each 0.001 gram of manganese.

The corrections necessitated by the presence of manganese varied between 6.3 and 15.6 calories. A similar correction was introduced on account of the presence of phosphorus. The total phosphorus in the cast irons varied between 1.120 and 1.424 per cent.; but the amount oxidized was from 0.325 to 0.656 per cent. So correction was made only for the phosphorus oxidized to phosphoric acid.



This would require a correction of 2.56 calories for 0.001 gram phosphorus, or from 9.5 to 18.8 calories for the various samples dissolved.

In determining the amount of heat evolved by the oxidation of the silicon present, the heat of solution of one gram of the sample was found, correction being made for the loss by radiation and gain by oxidation of cuprous chloride. The number of calories per gram of iron dissolved was calculated by dividing

<sup>1</sup> Thomsen's *Thermochemische Untersuchungen*, 3, 506.

<sup>2</sup> *Ibid.*, 3, 506; 2, 398; 2, 409; 3, 506; 2, 399.

this first figure by the per cent. of iron actually obtained in solution. From the figure thus derived was subtracted the amount of heat due to the manganese and the phosphorus oxidized with one gram of iron, in addition to 719.3 calories, the heat evolved by solution of one gram of pure iron. The remainder thus obtained was assumed to be the heat evolved by the oxidation of the silicon accompanying one gram of iron dissolved. From the heat due to the oxidation of the silicon accompanying one gram of iron, the number of calories for one gram of silicon was then calculated.

The calorimetric results obtained from the cast irons examined, are best shown in the subjoined table:

Grade of iron.	Per cent. of silicon.	Calories for one gram of sample.	Time in minutes required for solution.	Calories for one gram of iron dissolved.	Calories from oxidation of the silicon with one gram of iron.	Calories from oxidation of one gram of silicon.
Ferrosilicon.....	13.63	No action.				
Ferrosilicon.....	11.79	982.3	22	1163.9	444.6	3183
Silver-gray cast iron.....	6.16	820.4	7	968.9	215.2	2959
Silver-gray cast iron.....	4.69	765.6	6	900.4	150.2	2760
No. 2 soft cast iron.....	4.15	769.6	3	880.5	137.9	2904
No. 1 soft cast iron.....	3.55	765.9	4	873.1	133.6	3303
No. 1 foundry cast iron....	3.13	732.4	3	835.0	91.3	2561
No. 2 foundry cast iron....	2.56	720.6	5	817.9	79.5	2731
No. 3 foundry cast iron....	2.05	710.9	3	797.0	59.7	2598
Gray forge cast iron.....	1.40	690.5	5	781.1	42.4	2677
Mottled cast iron.....	0.89	672.7	11	741.3	-2.9	-298
Mottled cast iron.....	1.33	700.8	3	868.4	28.9	1989
Mottled cast iron.....	2.35	730.9	3	812.1	64.8	2822

A study of the above table seems to indicate the following facts:

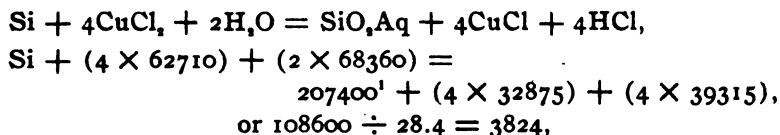
*First:* When either from a sufficiently high temperature of the blast-furnace at the time the iron is made or from the presence of a moderate amount of silicon, probably about one and four-tenths per cent., the carbon is nearly all in the graphitic or graphitic temper form; then the heat evolved by the oxidation of the silicon is proportional to the amount of silicon present.

*Second:* When from a low temperature in the furnace accom-



panied by low silicon the carbon is largely in the combined form; then the heat rendered sensible is very much diminished owing to the large amount of heat necessary to decompose the compounds of iron and carbon, or possibly compounds of iron, silicon, and carbon, or of carbon and silicon.

*Third:* Since from the equation:



we see that the oxidation of one gram of silicon alone evolves 3824 calories, and the results obtained by dissolving cast irons give a maximum of 3303 calories, it is evident that the compound of silicon with iron must have a very considerable heat of formation. This would indicate as a minimum for the equation:



If the mean of all the determinations, excluding the results on the two mottled irons containing high carbon, is taken, then the heat of formation would be increased to 27,700 calories.

*Fourth:* When the per cent. of silicon is sufficient or nearly sufficient to correspond with the empirical formula  $\text{SiFe}_s$ , the compound is insoluble in ammonium copper chloride. This is shown in the case of the higher silicon ferrosilicon.

These results are not in complete agreement with those obtained by F. Osmond,<sup>2</sup> but the differences may be ascribed either to the fact that he used samples of iron very low in all elements other than silicon, or to the fact that he used strictly neutral ammonium copper chloride instead of a slightly acid solution, which we have shown is much more active than the former.

<sup>1</sup> *Compt. rend.*, 113, 475—"Recherches calorimetriques sur l'etat du silicium et de l'aluminium dans les fers fondus," par F. Osmond.

<sup>2</sup> *Compt. rend.*, 113, 474.

ON THE OCCURRENCE OF HYDROGEN SULPHIDE IN THE  
NATURAL GAS OF POINT ABINO, CANADA ; AND  
ON A METHOD FOR THE DETERMINA-  
TION OF SULPHUR IN GAS MIX-  
TURES.<sup>1</sup>

BY FRANCIS C. PHILLIPS.

Received July 19, 1898.

ON the northern shore of Lake Erie, ten miles west from Buffalo, a narrow promontory extends for a distance of about two miles out into the lake. This promontory, known as Point Abino, forms the southern extremity of an important region of natural gas production from which a large part of the gas used in Buffalo at the present time is derived.

In 1892 a well was drilled by the Provincial Natural Gas Company near the extremity of Point Abino, to a depth of 600 feet. Gas was found in this boring at 550 feet below the surface, and again fifty feet deeper, or at the base of the Niagara limestone. The well has maintained its productiveness with little loss of pressure since the date of its drilling.

As regards chemical composition, the gas derived from this limestone at Point Abino differs in a remarkable manner from that which is usually found in the Devonian rocks of western Pennsylvania in the fact that it contains hydrogen sulphide, easily recognizable by its strong odor, by its action upon polished surfaces of silver and copper, and by the presence of sulphur dioxide among the products of its combustion. Two other wells on Point Abino yield gas of similar character (known locally as "sulphur gas") from the same geological formation.

It is common in drilling wells into the Niagara limestone in this region to find natural gas impregnated with hydrogen sulphide, sometimes occurring in small quantities, apparently stored in cavities from which it soon escapes and is exhausted ; in other cases the sulphur gas, when once it is tapped, may continue to flow for an indefinite period.

In cutting a sewer tunnel through the limestone, fifty to sixty feet under the city of Niagara Falls, and extending about one mile from Twenty-third street to the river, hydrogen sulphide

<sup>1</sup> Read at the Washington meeting of the American Chemical Society, December, 1897.

was frequently encountered, and was the cause of much inconvenience to the workmen, requiring the construction of ventilating shafts for its removal. The occurrence of this gas was always accompanied by a strong flow of dark-colored water.

Mr. W. A. Brackenridge, resident engineer for the Cataract Construction Company, informs me that hydrogen sulphide was found at a depth of about sixty feet in excavating for the wheel pit and tunnel shaft of this company at Niagara Falls. Patches of gypsum were often found about ten feet above the gas-bearing stratum. If this gas is allowed to come in contact with the polished metal surfaces about the power house they are rapidly blackened. Natural gas of the same character has been found near Fort Erie, at several places between Buffalo and Point Abino, and also at Port Colborne on Lake Erie, twenty miles west from Buffalo. Water well drillers state that they often strike sulphur gas at Chippewa, south of Niagara Falls. Southeast from Buffalo, from four to six miles, hydrogen sulphide occurs in the Niagara limestone of the West Seneca field, and at Alden, eighteen miles east from Buffalo. The sulphur gas is found in wells distributed over a territory extending irregularly for about forty miles east and west, and about twenty miles north and south.

Natural gas occurs in the region at three other horizons below the Niagara limestone; namely the Clinton limestone, the Medina sandstone, and the Trenton limestone, which latter rock was reached at a depth of 2940 feet in a well drilled six miles north of Point Abino. The Niagara limestone seems, however, to be the only one of these formations which yields gas containing hydrogen sulphide.

On September 2, 1896, I visited the well at Point Abino, and by the courtesy of Mr. E. Coste, engineer for the Provincial Natural Gas Company, was enabled to conduct some tests of the gas upon the spot and to collect samples for analysis. Of these tests made at the well and the results obtained, the following is a brief summary:

On leading the gas through an alkaline lead acetate solution, a heavy black precipitate was at once produced.

An ammoniacal cadmium chloride solution yielded a bright

yellow precipitate. The odor of hydrogen sulphide was very strong.

It seemed to be of interest to ascertain whether organic sulphur compounds were present among the hydrocarbons of this gas. Accordingly, a stream of the gas was caused to bubble through an alkaline lead acetate solution, in order to absorb hydrogen sulphide, and then through an alcoholic solution of mercuric chloride. The experiment was continued for six hours at the well. Methyl, as well as ethyl sulphide would have caused a precipitation in the mercuric chloride solution, if present even in very small quantity. The solution was found to remain clear. The absorbent solutions were returned to the laboratory to be further tested. The alkaline lead acetate solution was warmed upon a water-bath while a current of nitrogen was passed through the flask and into an alcoholic solution of mercuric chloride. In this latter solution no precipitate appeared, nor was any odor attributable to a sulphur ether observed. These tests seemed necessary, as a volatile sulphur ether might have condensed unchanged in the lead acetate solution during the passage of the gas in the trials which were made at the well. The nitrogen stream was used in order to evaporate any traces of such condensed sulphur compound, should there be any such, and carry its vapor over into the reagent solution.

In order to test for methyl mercaptan advantage was taken of the fact that its vapor is readily absorbed by an alkaline lead acetate solution and is again evolved when the liquid is acidulated and warmed. If the escaping vapors are led (by a nitrogen stream) into a solution of palladium chloride a cinnamon-colored precipitate is produced. This test was performed but the results were negative. The odor of mercaptans was not noticeable. It is of course possible that experiments with still larger volumes of gas might have disclosed the presence of traces of such organic sulphur compounds.

The vapors of methyl and ethyl sulphide, even if present in a gas in quantity insufficient to produce a precipitate in mercuric chloride solution, are absorbed by the solution, and impart to it their characteristic odor, so that this reagent may in such manner serve for the detection of very slight traces not otherwise recognizable.

In order to test for the presence of carbon monoxide the gas, as it flowed from the well, was passed (1) through lead acetate solution containing a large excess of sodium hydroxide to remove carbon dioxide and hydrogen sulphide, (2) through lime-water, in order to maintain control of the efficiency of the first solution, (3) through palladium chloride solution, and (4) through lime-water. When present in a gas mixture, even in traces, carbon monoxide is easily recognized by this method, the second lime-water becoming milky as a result of the oxidation of the carbon monoxide by the palladium chloride. The palladium chloride is simultaneously reduced, yielding a black precipitate of finely divided metal.<sup>1</sup>

In testing for free hydrogen the method I have described in the *American Chemical Journal*, 16, 259, was used. The gas freed from hydrogen sulphide and dried by phosphoric anhydride, was passed through a tube containing dry palladium chloride and then into silver nitrate solution. Dry palladium chloride is quickly reduced in the cold by free hydrogen, with formation of hydrogen chloride, which then produces its characteristic effect upon the silver nitrate solution.

The results of these tests, conducted at the well during about six hours, were negative, and the conclusion seems justified that carbon monoxide and free hydrogen do not occur in the Point Abino natural gas in recognizable quantity.

Tests for ethylene were made in small portions of the gas brought back to the laboratory for the purpose, but with negative results. Determinations of hydrogen sulphide were made by agitating a measured volume of the gas with an alkaline solution of lead acetate, in a bottle fitted with a rubber cork, traversed by inlet and outlet tubes having stop-cocks, and by a burette for the introduction of the reagent solution. This part of the work was carried out at the well, due account being taken of the temperature and barometric pressure. The bottle used was of 1890 cc. capacity. The precipitated lead sulphide was returned to the laboratory, its sulphur oxidized to sulphuric acid, and from the weight of barium sulphate obtained the proportion of hydrogen sulphide in the original gas was calculated.

<sup>1</sup> For details of this method as applied to natural gas see *American Chemical Journal*, 16, 275.

The results of four determinations made in this manner were 0.76, 0.73, 0.75, and 0.72 per cent.

Nitrogen was determined by combustion of a measured volume of the gas (about 150 cc.) over copper oxide, and measurement of the residual gas over mercury. This residue may include other inert gases besides nitrogen, but these have been classed together in the present analysis. The method used for collection of this inert residue is one requiring a somewhat complicated form of apparatus. Its details will be described in a later paper.

Carbon and hydrogen were determined gravimetrically, by weighing the carbon dioxide and water produced when a measured volume of the gas was burned over copper oxide. For this purpose glass cylinders holding from 350 to 400 cc. were filled with the gas at the well.

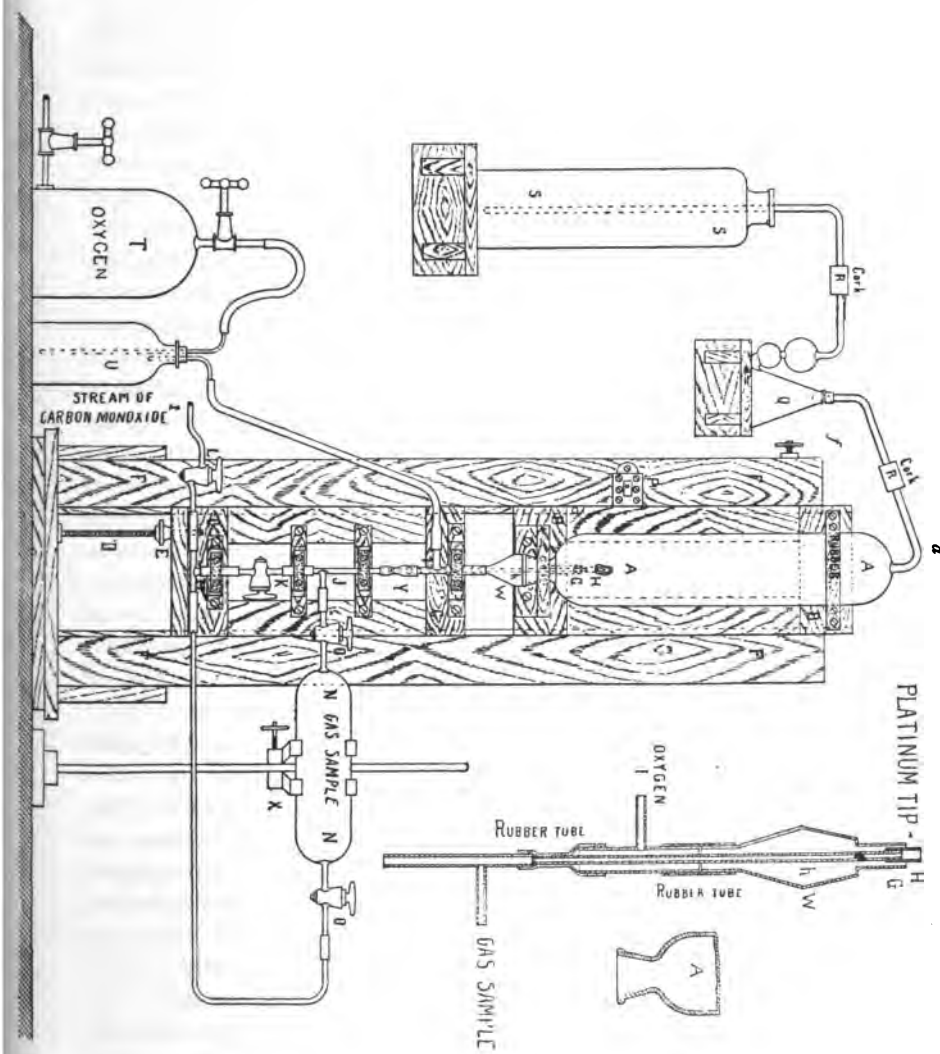
Results of analysis of natural gas from the Point Abino well.

	Per cent.
Hydrogen sulphide.....	0.74
Nitrogen .....	2.69
Carbon dioxide.....	trace
Carbon monoxide.....	0
Hydrogen .....	0
Ethylene .....	0
Hydrocarbons of the paraffin series .....	96.57
	<hr/> 100.00

The percentage composition of these paraffins by weight was :

	Per cent.
Hydrogen .....	24.10
Carbon .....	75.90
	<hr/> 100.00-

With a view to greater certainty in the determination of hydrogen sulphide it seemed desirable to employ a method by which the gas could be burnt, and the sulphur collected as barium sulphate. Accordingly, a process was devised for the combustion of a measured volume of the gas in an oxygen atmosphere, absorption of the sulphuric or sulphurous acid produced, and weighing of the sulphur as barium sulphate. Such a method is not new in principle, having been proposed by various authors for the determination of sulphur in gases. As adopted for use in the present instance the method may be described as follows :



The gas sample is contained in the vessel *N* (which may be replaced by a larger vessel if necessary). It is burnt from a narrow glass tube *h* surmounted by a roll of thin platinum foil *H*, in a light blown glass cylinder *A*, which is about forty cm. long and about ten cm. wide. The cylinder is closed below by a ground stopper *W*. This stopper is hollow and carries the narrow tube of about one and one-half mm. bore supplying the gas to be burnt. The narrow tube passes up through one of larger diameter which receives oxygen by way of the side tube *I* from a holder *T* and delivers it just below the flame of burning gas. As is shown in the sketch of the stopper *W* and its connections, the burner tubes are arranged concentrically, the oxygen issuing from the wide tube *G* and encircling the flame of the gas burning at the tip *H*. The rate of flow of the oxygen is approximately indicated by the rapidity of its bubbling through water in the bottle *U*. It seemed desirable to effect the expulsion of the gas from the sample vessel into the cylinder where it is to be burnt without the use of water, which by reason of its solvent power might absorb and partially remove those constituents of the gas which are to be determined. Mercury is out of the question. A gas appeared preferable and carbon monoxide was employed for the purpose. The carbon monoxide is contained in a gasholder and enters by the tube *L*, passing upward by *K* and *h* to the platinum tip *H*, where it is ignited. The combustion cylinder, which is mounted on the movable frame *BB*, is then lowered over the ignited carbon monoxide jet and clamped in position by the screw *f*. The outlet tube *a* is connected with the flask *Q* containing a solution of sodium carbonate to which some bromine has been added. The lower sliding frame *CC* can be raised or lowered by the nut *E* moving upon the fixed screw *D*. The carbon monoxide jet being ignited and the oxygen supply by way of *I* being adjusted so as to insure a steady flame, the stop-cocks *OO* are opened and then *K* is closed. The carbon monoxide then goes by way of the gas sample vessel to the jet, driving out the contained gas and carrying it into the combustion cylinder, where it is burnt. Many liters of gas may be burnt in this manner without danger of the flame becoming extinguished. The sodium hypobromite solution into which the products of the combustion have passed contains the sulphur



as sodium sulphate, and, after acidulation and evaporation, may be used for the determination of sulphur as barium sulphate. After the combustion is finished the apparatus is tilted down, the cylinder is rinsed, and the rinsings added to the contents of the flask *Q*. The large bottle *S* containing a few drops of bromine water, which is renewed from time to time during the process, is used to insure complete absorption of products of combustion of the sulphur. The connections *RR* consist of corks soaked in melted paraffin or spermaceti, rubber being objectionable on account of the sulphur which it contains.

The combustion of natural gas, or other gas rich in hydrogen, leads necessarily to the production of much water. This water is partly condensed at first, but as the temperature of the cylinder rises and evaporation is accelerated, the water vapor increases, and impairs the stability of the flame, which may flicker and become extinguished, even when the oxygen supply is apparently sufficient. The carbon monoxide, by diluting the products of combustion, tends to prevent condensation of steam and renders the flame more steady and more easily controlled. If very large volumes of gas are to be burned carbon monoxide cannot be used as it renders the process too slow, and in such case measurement of the gas must be effected by meter. No carbon monoxide is then required. Natural gas may be burned in this apparatus at the rate of a liter in twelve minutes.

Experiments have shown that the position of the gas sample vessel, whether vertically or horizontally placed, makes little difference, as the carbon monoxide rapidly mixes with the gas in the sample vessel and the two emerge together at the burner.

There appeared to be some danger that carbon monoxide made from oxalic acid by heating with sulphuric acid might contain volatile sulphur compounds. Carbon monoxide, prepared from chemically pure sulphuric acid and recrystallized oxalic acid, was found after passage through sodium hydroxide solution, to yield no sulphuric acid when ten liters were burned in the apparatus described.

Nitrous oxide may be substituted for oxygen in the process, and being readily obtainable in liquefied form, proves more convenient. During combustion in nitrous oxide higher oxides of nitrogen are formed in quantity sufficient to give a bright orange

color to the gaseous contents of the combustion cylinder. The conditions are then very favorable to the complete oxidation of gaseous sulphur compounds.

The Point Abino gas well was visited again on September 3, 1897, when the tests made a year ago were repeated, and other samples taken. Determinations of sulphur were made by the method of combustion above described. Determinations of hydrogen sulphide were also made by treatment of a known volume of gas at the well with alkaline lead acetate solution. The precipitated lead sulphide having been returned to the laboratory, its sulphur was converted by oxidation by means of potassium chlorate and hydrochloric acid into sulphuric acid, and precipitated and weighed as barium sulphate.

	By combustion in oxygen and weighing as barium sulphate. Percentage by volume.	By precipitation as lead sulphide and conversion into barium sulphate. Percentage by volume.
Hydrogen sulphide.....	0.80	0.77
	0.83	0.86
	0.82	0.80
	0.82	
	0.83	

The only important difference as regards composition between the natural gas from the Niagara limestone and that from the Devonian measures of western Pennsylvania consists, apparently, in the hydrogen sulphide which the former gas contains. If the sulphur compound be removed the residual gas is hardly distinguishable in composition from the natural gas of other regions. There appears to be reason for regarding the sulphur gas of Point Abino as natural gas which has received an addition of hydrogen sulphide derived from some local source. The same process which has produced natural gas in other regions has probably yielded this gas but the hydrogen sulphide which it contains may be derived from a different source, and may have been of more recent origin.

The occurrence of hydrogen sulphide in the Niagara limestone is no doubt connected with that of gypsum, which abounds so largely throughout the region. Gypsum has been quarried near Buffalo and is often found scattered through the limestone

in cavities. In artesian borings many alternations of limestone and gypsum are often encountered. Considerable masses of this mineral are found near Sherkston, north of Point Abino, and near Niagara Falls it occurs abundantly in the limestone.

If a genetic relationship exists, as is suggested by their association, it is difficult to determine whether the hydrogen sulphide, by oxidation in presence of limestone, has produced gypsum, or whether the gypsum has by decomposition yielded hydrogen sulphide. If hydrogen sulphide has undergone oxidation there seems to be reason to suppose that the process must have occasionally remained incomplete when occurring at great depths, and have resulted in the setting free of sulphur. Sulphur does not appear to occur native in the region. If the hydrogen sulphide has penetrated from greater depths to undergo oxidation in the higher strata it should be found more abundantly in the lower gas-bearing rocks, instead of being confined to the uppermost of these, the Niagara limestone.

On the other hand, the production of hydrogen sulphide from gypsum would seem to require an exposure to high temperature in presence of hydrocarbons—conditions which cannot have occurred. No one of the constituents of natural gas could, at temperatures existing in the stratified rocks of the region, have produced hydrogen sulphide by its action upon gypsum.

The Point Abino well produces, according to Mr. E. Coste, engineer for the Provincial Natural Gas Company, 1,000,000 cubic feet per day, and of this amount 7,000 cubic feet are hydrogen sulphide, corresponding to 600 pounds of sulphur, or 115 tons in one year. It is true that the well is not being drawn upon constantly up to its full capacity, but as it represents only one among the many outlets from which the sulphur gas escapes, it is evident that a very large quantity of sulphur, either in form of hydrogen sulphide, or burnt in furnaces to sulphur dioxide, is making its way annually into the atmosphere in the region of Buffalo and Niagara Falls.

# CERTAIN ALKALOIDAL PERIODIDES, AND THE VOLUMETRIC ESTIMATION OF ALKALOIDS AS HIGHER PERIODIDES.<sup>1</sup>

BY A. B. PRESCOTT AND H. M. GORDIN.<sup>2</sup>

## THE PERIODIDES IN RESPECT TO COMPLETENESS OF PRECIPITATION.

IN aqueous solutions of salts of the alkaloids, one of the most delicate of qualitative reagents is iodopotassium iodide. Wormley gives the limit of this precipitation, for the chief medicinal alkaloids, as from  $\frac{1}{100000}$  to  $\frac{1}{1000000}$  of a grain of the alkaloid in one grain of water; that is, from 0.0000013 to 0.0000007 gram in one cc. of water.<sup>3</sup> The precipitate is not appreciably soluble in excess of the reagent, an advantage over several other qualitative precipitations of alkaloids in general. In some cases the precipitate is appreciably soluble in excess of the alkaloidal salt, and this condition is one most easy to avoid. The potassium iodide solution of iodine was recommended as a reagent for alkaloids by Bouchardat, a medical writer in Paris, in 1839.<sup>4</sup>

As a volumetric solution, the decinormal solution of iodine with potassium iodide was first proposed by Wagner, in 1861,<sup>5</sup> and the decinormal strength is generally the most suitable for volumetric use.

## HISTORICAL AS TO THE FORMATION OF PERHALIDES IN GENERAL.

The formation of the alkaloidal periodides was first made a subject of systematic observation by Jörgensen, at Copenhagen,

<sup>1</sup> The portion of this article which concerns atropine was given in substance in this Journal, 20, 329, under the title "Atropine Periodides and Iodomercurates," by H. M. Gordin and A. B. Prescott (reprints). Also that concerning morphine and opium, except the "Results of Opium Assay," appeared in Kremers' *Pharmaceutical Archives*, June, 1898, 1, 121, under the title "A Volumetric Assay of Opium," by H. M. Gordin and A. B. Prescott (reprints).

<sup>2</sup> In the work of Research Committee D, Section 2, Committee on Revision of the Pharmacopoeia of the United States.

<sup>3</sup> Microchemistry of Poisons, 1885, Tabular View.

<sup>4</sup> Bouchardat, 1839: *Compt. rend.*, 9, 475; *L'Institut*, 7, 358. This precipitation, however, was proposed as an antidote for strychnine, in cases of poisoning of dogs. Further, see Donné: *Ann. chim. phys.* (2), 38, 82.

<sup>5</sup> R. Wagner: *Dingler's poly. J.*, 161, 40; *Ztschr. anal. Chem.*, 1, 102.

in 1869,<sup>1</sup> and the masterly researches of this Danish chemist, extending over nine years, afford a model of logical inquiry into chemical structure. A still wider study of all periodides and some other perhalides of organic bases was commenced in 1887 by Prof. Geuther<sup>2</sup> of Jena, but was cut short by his death in 1889. Among various periodides reported of later years have been picoline periodides by Wm. Ramsay in 1878;<sup>3</sup> cesium and rubidium periodides by Wells, and others, in 1893;<sup>4</sup> iodonium periodides by Victor Meyer in 1894;<sup>5</sup> sulphon periodides by Kastle in 1894;<sup>6</sup> periodides of diazo bodies by Hantsch in 1895;<sup>7</sup> halogen addition-products of the anilides by Wheeler and others in 1896-97;<sup>8</sup> perhalides of aliphatic amines by Norris in 1898;<sup>9</sup> mixed perhalides of alkyl anilines by Samtleben in 1898.<sup>10</sup>

In this laboratory since 1895 the perhalides and various double halides of pyridine have been obtained,<sup>11</sup> also the perhalides of caffeine,<sup>12</sup> and work on picoline perhalides is in hand. In the course of work upon an entirely different inquiry, a new order of perhalides has just been obtained, a periodide of brom-triphenylmethane.<sup>13</sup>

It is of interest to inquire what classes of compounds are liable to the formation of perhalides, and this inquiry has a special interest when it is proposed to estimate a single class of compounds, in vegetable drugs or their extracts, by formation of periodide. In general terms the reply is easily given, that

<sup>1</sup> Jørgensen, 1869-1878: *J. prakt. Chem.* (2), 2, 347, 433; 3, 145, 328; 14, 213, 356; 15, 65, 418; 16, 352; *Ber. d. chem. Ges.*, 2, 460.

<sup>2</sup> A. Geuther: *Ann. Chem. Pharm.* (Liebig), 240, 66-91, with lists of the organic periodides previously obtained.

<sup>3</sup> *Phil. Mag.* (5), 2, 269; 4, 241; 6, 19.

<sup>4</sup> *Am. J. Sci.* (3), 44, 42; 43, 17.

<sup>5</sup> *Ber. d. chem. Ges.*, 27, 1594.

<sup>6</sup> *Am. Chem. J.*, 16, 116.

<sup>7</sup> *Ber. d. chem. Ges.*, 28, 2754.

<sup>8</sup> *Am. Chem. J.*, 18, 85; 19, 672.

<sup>9</sup> *Am. Chem. J.*, 20, 51.

<sup>10</sup> A. Samtleben: *Ber. d. chem. Ges.*, 31, 1141.

<sup>11</sup> Prescott, the Periodides: *This Journal*, 17, 775; *Pharm. Rundschau*, 13, 233. Prescott and Trowbridge, Periodides of Pyridine: *This Journal*, 17, 859. Flinterman and Prescott, Dipyrindine Methylene Dibromide: *Ibid.*, 18, 28. Prescott, Pyridine Alkyl Iodides: *Ibid.*, 18, 91. Trowbridge, Periodides of Pyridine: *Ibid.*, 19, 322. Trowbridge and Diehl, Halides and Perhalides of Pyridine: *Ibid.*, 19, 558.

<sup>12</sup> Gomberg, Perhalides of Caffeine: *This Journal*, 18, 347-378.

<sup>13</sup> See paper by Gomberg read at Boston meeting of the American Chemical Society, August, 1898, and to be published in a subsequent number of this Journal.

periodides are limited to the organic basis, that is the more or less basal compounds of the nitrogen family of elements, and the inorganic alkalies. It is remarkable that the iodonium compounds yield periodides, which is quite in accord with the claim of Victor Meyer that in these bodies iodine itself strangely serves (with the benzene ring) as a base-forming element like a member of the nitrogen family. This view is supported further by Gomberg's production at this time of a periodide of a triphenylmethane derivative, as cited just above.

At present it seems highly improbable that any plant constituent other than the alkaloids, in the larger sense of organic bases, are of the sort of bodies which can form periodides in precipitation. Moreover, Wagner's reagent is used in a qualitative way along with plant analysis to an extent likely to call attention to any interference with its use for alkaloids. From the work of Wheeler it is evident that periodides may be formed by acid amides, but probably not by precipitation in dilute solutions. The formation of iodonium periodides, and a sulphone periodide, indicate that the limits of formation of perhalides cannot yet be declared, and it will be well for analysts to be watchful of new developments.

#### HISTORICAL AS TO ANALYTICAL USE OF PERIODIDES.

The volumetric use of a potassium iodide aqueous solution of iodine dates from Wagner in 1861,<sup>1</sup> and the solution in decimal strength of iodine is named Wagner's reagent.

This iodine solution was tried briefly by Schweissinger in 1885,<sup>2</sup> and at length by Kippenberger in 1895,<sup>3</sup> but both seem

<sup>1</sup> R. Wagner, 1861: *Ding. poly. J.*, 161, 40; *Ztschr. anal. Chem.*, 1, 102. Wagner wisely avoided washing the precipitate, but he failed to add the solution of alkaloid to that of iodine: "Man versetzt die Lösung der Basen, deren Menge man bestimmen will, mit überschüssiger Iod lösung, filtrirt und bestimmt in einem gemessenen Theil des Filtrats mit unterschweifligsaurem Natron das überschüssige Iod." As periodides had not then been prepared and analyzed, the iodine factors of Wagner were empirical, and, as the higher periodides are not invariably the sole products when iodine solution is added to the alkaloid solution, the factors adopted proved unsatisfactory. It is noteworthy that "Mayer's reagent" was so nearly contemporaneous with Wagner's, in publication. The potassium mercuric iodide method of volumetric estimation dates from 1862: *Proc. Am. Pharm. Assoc.*, 230; *Am. J. Pharm.*, 35, 20; *Chem. News*, 7, 159; 8, 177, 189. Of special American interest is Dr. F. Hoffmann's biography of Ferdinand F. Mayer as a New York chemist (*Pharm. Rundschau*, 1894, 12, 125), and of more general interest, Prof. Schaer's history of Mayer's alkaloid reagent (*Pharm. Rundschau*, 12, 142).

<sup>2</sup> *Arch. Pharm.*, 1885, 611.

<sup>3</sup> K. Kippenberger, 1895: *Ztschr. anal. Chem.*, 34, 317; 35, 407, 422.

to have obtained the lower periodides, at least in part, in their methods of estimation. The last-named author proceeded upon a volumetric deduction of a general formation of triiodides, and sought to so vary the conditions as to support the factor of a triiodide. In 1896, Gomberg,<sup>1</sup> along with his production of caffeine perhalides above referred to, established the volumetric estimation of caffeine in acidulated solutions as a pentaiodide, and this was used, with a method of extraction from Kola, throughout the work of Mr. Knox and one of us<sup>2</sup> upon the caffeine compound of kola, with complete satisfaction.

THE HIGHER PERIODIDES IN RESPECT TO CONSTANCY OF COMPOSITION.

The number of the periodides of pyridine is representative of the fact that most of the alkaloids of pyridine-derived constitution will form each more than one periodide, according to conditions. We find it is more expedient to secure the exclusive formation of the higher periodide, by needful conditions, than that of any other periodide obtainable. The higher periodides are not surpassed in completeness of precipitation, and they are sufficiently stable. At least this is true of those alkaloids included in this report. In future reports we desire to be able to give analyses of all the readily obtained periodides of each of the alkaloids reported upon in this article.

If we add the iodopotassium iodide solution to the solution of an alkaloidal salt, keeping from the beginning to the end the alkaloid in excess, it is generally the lowest periodide (in most cases a triiodide) that is formed, but if the order be reversed and the alkaloidal solutions added to the iodopotassium iodide solution, keeping all the time a large excess of iodine, it is generally the highest periodide that is formed. We have found this rule to hold good with atropine, strychnine, brucine, aconitine, and several other alkaloids. It was mainly the lower periodides of alkaloids that were made and described by Jørgensen; they are generally very stable and can be easily obtained in crystalline form by crystallization from some suitable solvent. As to the higher periodides, some of them are stable enough to be

<sup>1</sup> This Journal, 18, 331.

<sup>2</sup> Knox and Prescott: *Proc. Am. Pharm. Assoc.*, 44, 128; 45, 131; This Journal, 19, 63; 20, 34.

recrystallizable; many others are easily decomposed in solution into free iodine and lower periodides. Atropine enneaiodide belongs to the first class; strychnine heptaiodide and brucine heptaiodide belong to the second.

Following the above-mentioned rule, we have succeeded in obtaining an enneaiodide of atropine,  $C_{17}H_{23}NO_9HI.I_9$ ; a heptaiodide of strychnine,  $C_{21}H_{27}N_2O_7HI.I_7$ ; a heptaiodide of brucine,  $C_{23}H_{29}N_2O_7HI.I_7$ , and, as it is probable, a triiodide and a heptaiodide of aconitine. The tetraiodide of morphine, obtained by Jörgensen, is the only periodide of morphine that we have been able to make by precipitation.

These compounds are of the common order of alkaloidal hydriodide periodides. The single atom of iodine in the normal hydriodide is transposed by silver nitrate solution with precipitation, but does not respond to reducing agents. The rest of the iodine, being additive to the first atom of this element, is very easily taken up by reducing agents, such as sulphur dioxide, a thiosulphate, or powdered zinc.

#### PREPARATION OF THE HIGHER PERIODIDES IN PURITY FOR ANALYSIS.

The periodides, of which analysis is given in this paper, were all made according to the following method: One gram of the alkaloid was dissolved in about 200 cc. of water acidulated with sulphuric or hydrochloric acid, and the solution poured, in small quantities at a time, into 500 cc. of water containing one per cent. free iodine and one and a half per cent. potassium iodide. After shaking until the liquid became perfectly clear, the mother-liquor was removed in filtration by means of a pump, the precipitate well washed with cold water and dried first on porous plates and then in a vacuum over sulphuric acid. For the aconitine triiodide the order of mixing was reversed, and an excess of aconitine kept during the whole operation. After drying, the precipitate was recrystallized from alcohol. These periodides, so prepared, were subjected to analysis by the method given under atropine below, and as stated further under the several alkaloids, and from the results of the analysis, the volumetric factor of free iodine for each alkaloid was determined.



## ATROPINE ENNEAIODIDE AND ITS ANALYSIS.

The enneaiodide, obtained as above described, is a very dark brown, almost black powder, quite permanent in dry air, and has only a slight odor of iodine. It is very difficultly soluble in ether, chloroform, benzene, or carbon disulphide, but is soluble in alcohol, very freely when hot. In cold water it is insoluble; hot water decomposes it quickly; it is also decomposed by concentrated solutions of potassium iodide. At 90° C. it commences to give up iodine vapors, and at 140° C. melts to a dark liquid. To obtain it in crystalline form it is first washed with a little cold alcohol to remove traces of free iodine, and then dissolved in warm alcohol. On cooling it crystallizes out in dark-green prisms and leaflets, having the same properties as the non-crystallized body. In analysis we estimated the additive iodine volumetrically, and the total iodine both gravimetrically and volumetrically.

To estimate the additive iodine a small quantity of the enneaiodide is dissolved in very little alcohol, an excess of a standardized solution of sodium thiosulphate added, and the excess titrated back with a standard solution of iodine, using starch as the indicator.

For total iodine the substance is covered with an excess of powdered metallic zinc and some water, and then boiled gently for ten or fifteen minutes, taking care to prevent loss by spurt-ing; the mixture is then thrown upon a filter, and the containing flask and the filter are thoroughly washed with hot water. The iodine in the zinc iodide thus formed can either be estimated by precipitation with silver nitrate and nitric acid and weighing as silver iodide, or it is precipitated with an excess of a standardized solution of silver nitrate and the excess titrated back with a standard solution of ammonium thiocyanate, using ferric nitrate as indicator.

In the following analyses the standard silver nitrate solution was made to correspond with one per cent. of iodine, and the ammonium thiocyanate solution to correspond, cc. per cc., with the silver nitrate solution. The standard solution of iodine contained one per cent. of iodine, and the sodium thiosulphate solution corresponded, cc. per cc., with the iodine solution.

*Analysis of the atrophine enneaiodine not recrystallized:* In the

volumetric estimation for total iodine, 0.15225 gram required 12.2 cc. of the silver nitrate solution. For the iodine removed by reduction, 0.19255 gram required 13.7 cc. of the thiosulphate solution.

	Calculated for $C_{17}H_{23}NO_2.HI.I_2$	Found.
Iodine by reduction.....	70.88	71.15
Total iodine .....	79.74	80.13

In the gravimetric estimation from 0.218 gram 0.3207 gram silver iodide was obtained.

	Calculated for $C_{17}H_{23}NO_2.HI.I_2$	Found.
Total iodine .....	79.74	79.48

*Analysis of the atropine enneaiodide recrystallized from alcohol.*—

The methods employed were the same as with the non-recrystallized compound, and the standard solutions of the same strength.

In the volumetric estimation of total iodine, 0.12685 gram required 10.1 cc. of the silver nitrate solution. For the iodine removed by reducing agents, 0.23105 gram required 16.4 cc. of the thiosulphate solution.

	Calculated for $C_{17}H_{23}NO_2.HI.I_2$	Found.
Total iodine .....	79.74	79.62
Iodine by reduction.....	70.88	70.98

In the gravimetric estimation of total iodine, 0.2031 gram gave 0.30035 gram silver iodide.

	Calculated for $C_{17}H_{23}NO_2.HI.I_2$	Found.
Total iodine .....	79.74	79.90

The constitution of the compound is that of atropine hydriodide octaiodide. The alkaloidal hydriodide is formed, in the (acidulated) solution, by transposition of the alkaloidal salt taken with potassium iodide. Thus:  $C_{17}H_{23}NO_2.HCl + KI + I_2 = C_{17}H_{23}NO_2.HI.I_8 + KCl$ .<sup>1</sup> Therefore the ratio of the free iodine consumed, to the absolute atropine, is the ratio of  $I_8$  to  $C_{17}H_{23}NO_2$ , equal to ratio 1012.24 to 288.38, or of 1 of iodine to 0.2849 of atropine.<sup>2</sup> And 1 cc. of decinormal iodine solution consumed is equivalent to 0.0036048 gram of the atropine. *This decinormal*

<sup>1</sup> For experimental verification of this equation, see a later paragraph in this paper.

<sup>2</sup> The atomic weights taken were those of L. Meyer and K. Seubert,  $H = 1$ .

*factor* was found to hold good under the control estimations reported further on.

OTHER ATROPINE PERIODIDES, AND ATROPINE MERCURIC IODIDES.

Having obtained the enneaiodide of atropine, it was natural to suppose the existence of a heptaiodide, with probability of a complete series from the triiodide to the enneaiodide. And in fact in the course of our work we once obtained this heptaiodide. But our efforts to determine the exact conditions necessary for the formation of this body have so far not been successful. Whether additional quantities of atropine will make the precipitate take up more atropine and become a lower periodide we shall try to determine by later experiments. On the other hand, when the order is reversed and the iodine solution is added to the atropine solution, it is always a lower periodide that is formed; but whether on continued addition of the iodine the precipitate will take up more of it and become a higher periodide, we cannot say as yet.

The easiest way to obtain the periodides of atropine is to use chloroform as a solvent. On adding twenty grams atropine to a warm solution of thirty grams iodine in chloroform (500 cc.) the enneaiodide crystallizes out very soon in the shape of small, shining, dark green crystals. If these be removed by filtration, the mother-liquor will give several successive crops of the dark blue pentaiodide, and at last a crop of the brownish-red triiodide.

*Atropine mercuric iodides* are best known as products of precipitation of atropine salts by Mayer's reagent, the solution of potassium mercuric iodide.<sup>1</sup> We find that they can be obtained by shaking the alcoholic solution of a periodide with metallic mercury and warming the mixture. Double iodides of atropine and mercury can also be made by mixing theoretical quantities of atropine and iodine, adding a little alcohol and an excess of mercury, slightly warming, and shaking till the color of iodine disappears. If the higher periodides of atropine be used in the preparation of this double iodide of atropine and mercury there

<sup>1</sup> Groves, 1859: *Quar. J. Chem. Soc.*, 11, 97, 188. F. F. Mayer, 1862: *Am. J. Pharm.*, 35, 20; *Chem. News*, 7, 159; 8, 177, 189. Prescott, 1880: *Am. Chem. J.*, 2, 294; 14, 606.

is always separation of mercurous iodide; but if theoretical quantities of atropine and iodine be used there is no separation of mercurous iodide. The formula of this double iodide of mercury and atropine, as shown by our analysis, seems to be  $C_{17}H_{21}NO_3 \cdot HI \cdot HgI_2$ . It resembles in composition several other double iodides of alkaloids and mercury obtained by Groves by a different method, and agrees in proportion with the strychnine compound, not with the morphine or quinine compound obtained by one of us in 1880.<sup>1</sup> But besides this double iodide we also obtained another having the composition  $(Atrop. HI)_2 \cdot HgI_2$ . It was made by treating a solution of the  $(Atrop. HI) \cdot HgI_2$  in diluted alcohol with an excess of potassium iodide. From the liquid obtained by shaking an alcoholic solution of atropine and iodine with mercury the monoatropine hydriodide mercuric iodide crystallizes out in shining, yellow crystals, melting at  $80^\circ$  to  $90^\circ$  C., difficultly soluble in ether or chloroform, partly soluble in hot water, and very soluble in warm alcohol. The diatropine hydriodide mercuric iodide obtained, as said above, by the action of potassium iodide on the mono compound, crystallizes in perfectly white, silky needles, which, on being dried, assume a yellowish tint. They melt at  $98^\circ$  to  $99^\circ$  C., are very easily soluble in warm alcohol, and quite soluble in hot water.

The analysis for mercury and for iodine in these bodies can be made in different ways, but the best results are obtained by a modification of the method of Risse.<sup>2</sup> The mercury and the iodine are determined in two separate portions. For mercury the substance is dissolved in a little warm alcohol and a little water added; the solution is then acidulated with a few drops of dilute hydrochloric acid and saturated with hydrogen sulphide. The mercuric sulphide is then dried and weighed in the usual way. For the determination of iodine the substance is treated with a hot solution of potassium hydroxide (1:10), diluted with water, filtered, and when completely cold, neutralized with acetic acid. The iodine is now precipitated with silver nitrate and nitric acid, and determined as silver iodide in the usual way.

In the following analyses the standard silver nitrate solution

<sup>1</sup> Prescott: *Am. Chem. J.*, 2, 297.

<sup>2</sup> *Ann. Chem.* (Liebig), 107, 223.

was made to correspond with one per cent. of iodine, and the ammonium thiocyanate solution to correspond, cc. per cc., with the silver nitrate solution. The standard solution of iodine contained one per cent. of iodine, and the sodium thiosulphate solution corresponded, cc. per cc., with the iodine solution.

*Analyses of the Double Salts of Atropine Hydriodide and Mercuric Iodide:* 0.2632 gram of the monoatropine hydriodide mercuric iodide gave 0.0699 gram mercuric sulphide, and 0.30445 gram of the substance gave 0.24785 gram silver iodide.

	Calculated for $C_{17}H_{23}NO_3.HI.HgI_2$ .	Found.
Mercury.....	23.03	22.89
Iodine.....	43.74	43.98

Of the diatropinehydriodide mercuric iodide, 0.1798 gram gave 0.032 gram mercuric sulphide, and 0.257 gram of the substance gave 0.18885 gram silver iodide.

	Calculated for $(C_{17}H_{23}NO_3.HI)_2.HgI_2$ .	Found.
Mercury.....	15.58	15.34
Iodine.....	39.46	39.70

#### STRYCHNINE HEPTAIODIDE AND ITS ANALYSIS.

The heptaiodide of strychnine is a dark brown powder, hardly soluble in ether, chloroform or benzol, and requires considerable alcohol for solution. It cannot be recrystallized, as it is easily decomposed into free iodine and the triiodide.<sup>1</sup>

The total iodine was determined by silver nitrate after reduction with zinc and ammonia. The additive iodine was estimated after dissolving the periodide in alcohol, by titrating with thio-sulphate.

For total iodine :

1. 0.3816 gram of the periodide gave 0.51345 grams silver iodide.
2. 0.30625 gram gave 0.4112 gram silver iodide.

	Calculated for $C_{21}H_{29}N_3O_2.HI.I_3$ .	Found.
1 .....	72.66	72.70
2 .....	.....	72.54

For additive iodine :

1. 0.1754 gram of the substance was found to contain 0.109 gram free iodine.
2. 0.17805 gram contained 0.111 gram free iodine.

<sup>1</sup> A triiodide was reported by Tilden in 1865 (see Geuther's lists, *loc. cit.*).

	Calculated for $C_{21}H_{27}N_3O_9.HI.I_2$	Found.
1 .....	62.28	62.14
2 .....	....	62.34

Six atoms iodine coming from the free iodine of the iodo-potassium iodide solution, we get the ratio:  $I_2$  to  $C_{21}H_{27}N_3O_9$ , or 1 of iodine to 0.439 of strychnine absolute. This gives the *decinormal factor* (the value of one cc. of decinormal iodine solution) as 0.0055547 for strychnine.

#### BRUCINE HEPTAIODIDE AND ITS ANALYSIS.

This was made according to the general method already given, by pouring a half per cent. solution of brucine acidulated with hydrochloric acid into a large excess of a one per cent. solution of iodine. In appearance and solubility it closely resembles the heptaiodide of strychnine, but it exercises a strong reducing action on silver salts, so that its analysis for total iodine is best accomplished by the aid of nitrous acid and bisulphide of carbon as described under the head of morphine tetraiodide and its analysis.

For total iodine :

1. 0.1916 gram of the periodide was found to contain 0.13229 gram total iodine.
2. 0.2395 gram of the periodide contained 0.16536 gram total iodine.

	Calculated for $C_{15}H_{16}N_2O_4.HI.I_7$	Found.
1 .....	69.21	69.04
2 .....	....	69.04

For additive iodine :

1. 0.1622 gram of the substance contained 0.096006 gram free iodine.
2. 0.192 gram contained 0.114 gram free iodine.

	Calculated for $C_{15}H_{16}N_2O_4.HI.I_4$	Found.
1 .....	59.32	59.19
2 .....	....	59.37

For brucine, therefore, the ratio is  $I_2$  to  $C_{15}H_{16}N_2O_4$ , or 1 of iodine to 0.5179 of anhydrous brucine. And 1 cc. of strictly decinormal solution of iodine indicates 0.0065530 of brucine, the *decinormal factor*, subjected to trial as stated later.

#### MORPHINE TETRAIODIDE AND ITS ANALYSIS.

Two samples were made. In the first, one gram of morphine

dissolved in 200 cc. acidulated water was added to a solution of five grams iodine and seven and one-half grams potassium iodide in 500 cc. water, the mixture shaken till the supernatant liquid was perfectly clear, and the precipitate washed and dried in vacuum. In the second, two grams iodine and three grams potassium iodide were dissolved in 200 cc. water and the solution poured slowly into a solution of morphine containing three grams morphine in 600 cc. acidulated water. The analysis, as given below, showed that the precipitate in both cases was the same; namely,  $C_{17}H_{19}NO_8HI.I_2$ . This compound, morphine tetraiodide, was made known by Jørgensen in 1870.<sup>1</sup> We find it to be the only periodide formed by morphine under any of the conditions of this precipitation from aqueous solutions.<sup>2</sup> It is notable that in this periodide the base as a monamine holds an even number of atoms of total iodine. The periodide precipitate of morphine is practically insoluble when the iodine is in excess, though appreciably soluble when the morphine is in excess, as it is in pure water, the more so if strongly acidulated.

*In the analysis* of the morphine periodide, the precipitate is to be collected and quickly washed with water by the aid of the pump, and then dried in vacuum over sulphuric acid to a constant weight. The additive iodine is readily determined, in a weighed portion, by dissolving in alcohol and titrating with a standard solution of sodium thiosulphate as stated in previous paragraphs. The total iodine determination in this compound gives special difficulty, as neither the sulphur dioxide nor the powdered zinc, previously used in this laboratory for analytical reduction of periodides, works well with morphine periodide, but the following procedure suffices. The periodide is covered with powdered zinc and stronger water of ammonia and set aside half an hour, the mixture is then heated on the water-bath till all the ammonia is driven off, avoiding loss by spurting. A little water is now added and the mixture boiled about ten minutes. The whole is filtered into a separator of about 500 cc.

<sup>1</sup> *J. prakt. Chem.* (2), 2, 437.

<sup>2</sup> The present hypothesis of structure of periodides would imply, therefore, that the compound is a dimorphine octaiodide (This Journal, 17, 780; 19, 331). A lower periodide of morphine was obtained by evaporation of an alcoholic solution containing excess of morphine, by H. R. Bauer (*Arch. Pharm.* [3], 5, 289-309).

capacity, the excess of zinc well washed with hot water, and water added to make 200 or 300 cc. When perfectly cold, the mixture is acidified slightly with very dilute sulphuric acid, then twenty cc. of carbon disulphide are poured into the separator, and ten to twelve drops of concentrated sulphuric acid *saturated with nitrous acid* are added. The separator is closed and shaken, and the solution of iodine in carbon disulphide carefully run out upon a wetted filter. Fresh carbon disulphide is added in the separator and the separation repeated till all the iodine is removed. The iodine is now washed on the filter, first with water, then with a very weak solution of sodium bicarbonate. It is then run into a flask, and thirty cc. of a solution of sodium bicarbonate, five grams to the liter, are added. Finally the iodine is titrated with the standard solution of sodium thiosulphate. The results were as follows :

I. Iodine in excess :

0.2692 gram gave 0.13 gram additive iodine and 0.2732 gram gave 0.174311 gram total iodine.

	Calculated for $C_{17}H_{19}NO_2.HI.I_2$	Found.
Additive iodine.....	48.02	48.29
Total iodine .....	64.03	63.80

II. Morphine in excess.

0.3155 gram were found to contain 0.152832 gram additive iodine and 0.2708 gram contained 0.172076 gram total iodine.

	Calculated for $C_{17}H_{19}NO_2.HI.I_2$	Found.
Additive iodine.....	48.02	48.44
Total iodine .....	64.03	63.54

For morphine the ratio is  $I_2$  to  $C_{17}H_{19}NO_2$ , or ratio of 379.59 to 284.38, that is 1 of free iodine consumed to 0.74918 of morphine, anhydrous. And one cc. of strictly decinormal solution of iodine corresponds to 0.0094794 gram of morphine.

ACONITINE HEPTAIODIDE (?) AND ITS ANALYSIS.

The alkaloid we used was obtained from Merck and marked "From Acontum Napellus, crystallized, pure." This periodide was made according to the general plan of obtaining the highest periodide of an alkaloid.

For additive iodine 0.2588 gram contained 0.126886 gram free



iodine and 0.1471 gram contained (by nitrous acid method) 0.082271 gram total iodine.

	Calculated for $C_{33}H_{43}NO_{13} \cdot HI \cdot I_2$	Found.
Additive.....	49.58	49.03
Total.....	57.85	55.93

We make our calculations upon the aconitine formula of Dunstan.<sup>1</sup> The formula of Freund<sup>2</sup> though distinctly different in constitution, gives but slightly different molecular weight. Other proposed formulas approach the same molecular weight.  $C_{33}H_{43}NO_{11} = 643.55$  (Freund).  $C_{33}H_{43}NO_{11} = 645.54$  (Dunstan).  $C_{33}H_{43}NO_{11} = 647.54$  (Jürgens).  $C_{33}H_{43}NO_{11} = 643.54$  (Wright and Luff).

An insufficiency of the aconitine in our hands prevented our making duplicate estimations. With both the higher and the lower periodide, it is to be seen that the total iodine found is somewhat too low for the calculated quantity of this element, calculating for heptaiodide and triiodide, respectively. The additive iodine in both cases falls below calculation, but not enough below to discredit the formulas. When we return to these estimations with a larger supply of the alkaloid we shall find whether the instability of aconitine will prevent constant results in analysis of the higher periodide or not.

#### ACONITINE TRIIODIDE (?).

This was made by adding a one per cent. solution of iodine to an acidulated solution of aconitine, leaving the latter in excess, and recrystallizing the precipitate from alcohol. Thus obtained it forms beautiful brown-red crystals, very soluble in alcohol, insoluble in water and hardly soluble in ether, benzol, or chloroform. Melting-point  $211^{\circ}$ – $212^{\circ}$  C.

For additive iodine :

0.01773 gram of the substance contained 0.042352 gram free iodine.

	Calculated for $C_{33}H_{43}NO_{13} \cdot HI \cdot I_2$	Found.
	24.69	23.89

For total iodine by the aid of nitrous acid and bisulphide of carbon, as given under the head of morphine.

<sup>1</sup> *J. Chem. Soc.*, 67, 459.

<sup>2</sup> *Ber. d. chem. Ges.*, 27, 722.

0.2111 gram contained 0.07505 gram total iodine.

Calculated for  
 $C_{12}H_{18}NO_{12} \cdot HI \cdot I_2$

37.03

Found.

35.56

#### VERIFICATION OF THE EQUATION FOR THE IODINE FACTOR.

Partly from the fact that Kippenberger<sup>1</sup> has proposed a different reaction in the formation of periodide precipitates, and for other reasons, we thought it advisable to prove irrefutably that the iodide of potassium of the iodine solution takes an active part in the reaction by which the atropine enneaiodide, as an example, is formed and gives off an amount of iodine which is just equal to the amount of the normal iodine of the enneaiodide.

We proceeded in the following manner: We first determined the strength of our iodine solution with regard to free iodine; this was done by means of a sodium thiosulphate solution of known strength. We then took ten cc. of this iodine solution and determined the total amount of iodine, free as well as bound to potassium, by shaking them in a flask with an excess of powdered metallic zinc till the color of iodine disappeared, filtering the solution of zinc iodide and potassium iodide thus obtained, washing the flask and the excess of zinc with hot water and precipitating the iodides in the filtrate with silver nitrate and nitric acid. From the weight of silver iodide washed and dried in the usual way, we calculated the amount of total iodine present in our iodine solution. By subtracting the amount of free iodine from that of the total iodine we obtained the amount of iodine present in our solution as potassium iodide. We thus found that the iodine solution contained one per cent. free iodine and 1.2312 per cent. combined iodine.

We then put forty cc. of this iodine solution in a 100 cc. measuring flask, added twenty cc. of a three-tenths per cent. solution of atropine alkaloid, and after shaking well, diluted the liquid in the flask to 100 cc. We now took two vials and in each filtered off twenty-five cc. from the flask. In the first vial, the amount of free iodine titrated back with sodium thiosulphate was found to be 0.0465. From this it is easy to deduce that the twenty cc. of the three-tenths per cent. atropine solution consumed 0.214

<sup>1</sup> *Ztschr. anal. Chem.*, 35, 10; 34, 317. On this question also see Gomberg, 1896: *This Journal*, 18, 332.

gram of the free iodine. In the second vial the total iodine was determined in the same way as described above, and the quantity of silver iodide was found to be 0.3023 gram, which shows that after the treatment with atropine the liquid contained 1.633 per cent. total iodine. From these data we deduce that the twenty cc. of the atropine solution have taken up 0.02528 gram iodine from the bound iodine. As the twenty cc. of atropine solution contained 0.06 gram atropine we find for 100 parts of precipitated enneaiodide

	Found. Per cent.	Calculated. Per cent.
Atropine .....	20.05	20.26
Iodine taken from the free iodine of the iodine solution.....	71.50	70.88
Iodine from the iodine bound as KI..	8.45	8.86

We see that in aqueous acidulous solutions the potassium iodide takes an active part in the reaction by joining in a yield of hydriodic acid for the normal hydriodide of the alkaloid, necessary to hold the additive iodine of the periodide. When carbon disulphide or carbon tetrachloride is used as a solvent for the atropine and the iodine, no periodide seems to be formed, possibly for the reason of there being no generation of hydriodic acid for the making of hydriodide. As to the formation of the periodides in chloroformic solution of atropine and iodine, it might possibly be explained by the substituting action of iodine either upon the chloroform or upon a side-chain of the atropine.

The direct substitution of iodine for some of the hydrogen in these bodies might, in this case, be made possible by the presence of the natural base, which combines with the hydriodic acid when formed by such a substitution. Part of the atropine would then act in a manner similar to that of mercuric oxide, which is usually employed in the iodizing of hydrocarbons. An analogous case we have in the easy substitution of iodine for some of the hydrogen in aniline, a part of which combines with the hydriodic acid, which is set free through the substitution of iodine for hydrogen in another part. At any rate we shall endeavor to determine the by-products formed when atropine enneaiodide is produced in chloroformic solutions.

## PROCEDURE IN THE VOLUMETRIC METHOD.

The general mode of procedure in the estimation of the strength of an aqueous solution of an alkaloidal salt is as follows: To about ten cc. of decinormal iodine solution diluted with a little water, one cc. of the acidulated alkaloidal solution is added, and the mixture well shaken for a few minutes. Should the precipitate separate out very quickly, and the clear supernatant liquid have only a light yellow or greenish color, or be altogether colorless, the alkaloidal solution is too strong and must be diluted, till after a few trials the clear supernatant liquid retains a very dark red color after the separation of the precipitate. The acidulated alkaloidal solution is then made up to a given volume, and ten or fifteen cc. of it are run from a burette into a graduated vessel, into which has been previously put twenty-five or thirty cc. decinormal iodine solution diluted with a little water. The mixture is then made up to a given volume and shaken till the supernatant liquid is perfectly transparent, and is of a very dark red iodine color. This point is very important, and should the clear liquid not have this dark red color, the experiment with most alkaloids (except morphine and possibly some others) should be repeated, putting more decinormal iodine into the graduated vessel, or decreasing the number of cc. of the alkaloidal solution. It would not do to add more decinormal iodine to the same mixture, as the iodine must be in large excess during the whole operation, in order to prevent the formation of lower periodides, which once formed, might not take up fresh iodine and form higher periodides. Only with morphine, which in such solutions forms but one periodide, these precautions are unnecessary. When the liquid has become perfectly clear, an aliquot portion of it is filtered off, and the excess of iodine determined by standard sodium thio-sulphate. From these data are obtained the quantity of iodine consumed. This quantity of iodine, multiplied by the "ratio of alkaloid to 1 of iodine," gives the quantity of alkaloid sought. If preferred, but generally with less convenience to the chemist, the number of cubic centimeters of decinormal solution of iodine consumed may be multiplied by the "alkaloidal factor of 1 cc.  $\frac{N}{10}$  I sol."

VERIFICATION OF THE IODINE FACTORS BY VOLUMETRIC  
CONTROL.

*For Atropine.*—In the following estimations of the strength of atropine solutions, both the iodine solution and the sodium thio-sulphate solution were strictly decinormal. Of the iodine solution twenty or twenty-five cc. were put into a 100 cc. measuring flask and atropine solutions of known strength run in from a burette, and the operation continued as described above. When the supernatant liquid was perfectly transparent the flask was filled up to 100 cc. and fifty cc. were filtered off. In these fifty cc. the excess was determined by means of the tenth-normal thiosulphate solution, and the strength of the atropine solutions calculated by using the factor 0.0036048 for every cubic centimeter of decinormal iodine used up.

	Actual strength. Per cent.	Number of cc. of the atropine solution taken.	Number of cc. of the tenth-normal iodine used up.	Results in strength. Per cent.
1 .....	0.50	12	15.6	0.47
2 .....	0.40	15	14.9	0.36
3 .....	0.30	17	13.2	0.28
4 .....	0.25	12	10.0	0.28

*For Strychnine.*—To test the correctness of the ratio of 1 of free iodine to 0.4390 of strychnine, two solutions were prepared, one of one per cent., the other of 0.612 per cent. of the alkaloid. The estimations, by the volumetric method, gave results as follows :

	Actual strength. Per cent.	Strychnine solution taken. cc.	Iodine consumed.	Results obtained. Per cent.
1 .....	1.0	3	0.07	1.026
2 .....	0.612	7	0.191	0.633

*For Brucine.*—Two solutions of the alkaloid were made, and estimated volumetrically, calculating by the ratio 1 part of iodine to 0.5179 part of anhydrous brucine, with these results :

	Actual strength. Per cent.	Brucine solution taken. cc.	Iodine consumed.	Results obtained. Per cent.
1 .....	1.0	10	0.193	0.999
2 .....	0.5	10	0.096	0.497

*For Morphine.*—Three standard solutions were made of strengths in anhydrous alkaloid as below tabulated. This was done by weighing a good article of well-crystallized morphine,

free alkaloid, as  $C_{11}H_{19}NO_3 \cdot H_2O$ . The results were calculated by the ratio 1 of iodine to 0.74918 of morphine, absolute.

	Strength in per cent.	Morphine solution. cc.	Iodine solution. cc.	Iodine consumed.	Result in per cent.
1.....	0.518	10	20	0.070116	0.525
2.....	0.259	10	20	0.034272	0.257
3.....	0.100	10	20	0.014020	0.105

THE IODINE FACTORS OF THE ALKALOIDS SO FAR  
DETERMINED.

Higher periodide formed.	Ratio of alkaloid to one of iodine.	Alkaloid factor of one cc. tenth-nor- mal iodine solution.
Atropine, $C_{17}H_{23}NO_3 \cdot HI \cdot I_2$ .....	0.2849	0.0036048
Strychnine, $C_{21}H_{27}N_2O_2 \cdot HI \cdot I_2$ ...	0.4390	0.00555467
Brucine, $C_{23}H_{29}N_2O_4 \cdot HI \cdot I_2$ .....	0.5179	0.00655299
Morphine, $C_{17}H_{19}NO_3 \cdot HI \cdot I_2$ ...	0.74918	0.00947937
Aconitine, $C_{33}H_{45}NO_{12} \cdot HI \cdot I_2$ ....	.....	.....

By Gomberg in 1896 :<sup>1</sup>

Caffeine, $C_8H_{10}N_4O_2 \cdot HI \cdot I_2$ .....	0.3834	0.00485
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APPLICATION IN ASSAY OF CRUDE MEDICINAL DRUGS.

We have made estimations of total alkaloids in *nux vomica*, and in *belladonna*, by the periodide volumetric method, after extraction of the alkaloid in several ways, and have obtained satisfactory results. We have work in hand by which we hope to reach more expeditious methods of extraction. Among the menstrua under experimentation, are a saturated solution of gaseous ammonia in ether, a chloroformic solution of ammonia,<sup>2</sup> and similar agents.

A VOLUMETRIC ASSAY OF OPIUM.

The morphine was estimated as periodide, after successive treatment with benzol, amyl alcohol or acetone, and lime-water.

This method proceeds upon the following plan: The opium alkaloids are set free by action of ammonia with certain solvents. The free narcotine, papaverine, codeine, and thebaine are then removed by percolation with benzene, after which the morphine is taken out by percolation with acetone,<sup>3</sup> in which the morphine

<sup>1</sup> This Journal, 18, 339.

<sup>2</sup> Suggested by Siedler and Thoms: *Ber. d. pharm. Ges.*, 1898, 28.

<sup>3</sup> Instead of acetone there may be used pure amyl alcohol, boiling between 128° and 132° C., and leaving no residue upon evaporation below the boiling-point.

is sufficiently soluble. The acetone is then evaporated off, and the residue taken up with lime-water, which completely dissolves and purifies the morphine. It remains to filter the lime solution, acidulate it with hydrochloric acid, and estimate the morphine as periodide by titration as already detailed in this paper.

In the percolation of the opium with different solvents to separate the morphine, we depend upon two things, (1) the preparing of the opium powder by digestion with the ammonia and the solvents and then drying, and (2) an admixture with dried common salt in transferring to the percolator.

*The Materials for the Assay.*—Opium in fine powder (No. 60 or finer), one gram; stronger ammonia water; alcohol, ether, chloroform, pure benzene (crystallized); acetone, boiling between  $54^{\circ}$  and  $58^{\circ}$  C., about 200 cc.; some good lime-water; ordinary common table salt, about twenty grams; some diluted hydrochloric acid (ten per cent.); decinormal solution of iodine with potassium iodide (Wagner's reagent), and sodium thiosulphate solution standardized with the solution of iodine.

*Directions for the Assay.*—Of the opium in fine powder one gram is weighed into a small mortar or deep dish, such as can be well covered with admission of a small pestle.<sup>1</sup> A mixture is made of five cc. of stronger ammonia water, five cc. of alcohol, twenty cc. of ether, and ten cc. of chloroform. The opium is rubbed up with two or three cc. of this mixture, to make a uniform paste, using a pestle that can be left in the dish when it is covered. The covered dish is now put aside for about three hours, from time to time moving the dish gently; about fifteen grams of well dried and finely powdered common salt are now added and carefully mixed into the mass. Then the dish is left open in a warm place, of  $30^{\circ}$  to  $35^{\circ}$  C., for two or three hours, when it is placed in a desiccator containing sulphuric acid and a dish of paraffin, a vacuum desiccator being preferable, until the mixture is perfectly dry as shown by the looseness of the powder under the motion of the pestle. If left over night it is sufficient. The entire contents of the dish are now transferred to a little glass percolator of about one and three-tenths centimeters

<sup>1</sup> A screw-top ointment jar of mortar-shaped bottom and four or six ounces capacity serves very well.

(one-half inch) inner diameter and twenty-two centimeters (nine inches) length,<sup>1</sup> rubbing out the dish twice with a little more of the dried common salt. The mass is now percolated with the benzene, until the percolate is colorless, and until upon evaporating one or two drops of the percolate in a watch-glass, taking up the residue with four or five drops of acidulated water and adding a drop or two of Wagner's reagent, no turbidity appears (removal of alkaloids other than morphine). A shallow dish is now set under the percolator, and pure acetone used to continue the percolation to complete exhaustion, as found by evaporating ten drops of the percolate on a watch-glass, taking up the residue with two or three drops of acidulated water, and adding a drop or two of Wagner's reagent, when no turbidity at all should appear. Usually as much as 200 cc. of acetone are required. The acetone is now evaporated, at a temperature not exceeding 45° C., to complete dryness. The residue when cool is rubbed up with good fresh lime-water, the solution poured without filtering into a graduated stoppered cylinder of 100 cc., the dish washed four or five times with portions of lime-water, to fully clean the dish, when lime-water is added to make the volume 100 cc. The cylinder is now securely stoppered and well shaken for half an hour. Of the mixture enough is now filtered into another graduated cylinder, with glass stopper, to make up a filtrate exactly fifty cc. To this liquid is added diluted hydrochloric acid (ten per cent.) to just perceptible acidulation, and the tenth-normal iodine solution is slowly run in from the burette while gently shaking the cylinder until precisely twenty-five cc. have been added. Water is added to any convenient mark of the cylinder, which is then stoppered securely and shaken vigorously and continuously (for about twenty minutes) until, on standing a minute or two, the supernatant liquid (of a pronounced iodine-red color)<sup>2</sup> is perfectly clear and transparent. The liquid is now filtered off so as to take just one-half the volume of the filtrate. In this half of the liquid the excess of iodine is titrated back with the tenth-normal sodium thiosulphate solution, using starch as an indicator. The number of cubic centimeters of the thiosulphate solution multiplied by two,

1 The tube of a one-ounce syringe does very well.

2 If the liquid does not have this red color, it must be because of a lack of the indispensible excess of the iodine, of which an additional quantity should be added.



is subtracted from twenty-five, the number of cubic centimeters of iodine solution used. The remainder is now multiplied by the factor 1.89586 ( $0.0094793 \times 2 \times 100$ ), the product being the percentage of morphine in the powdered opium as weighed.

The precautions most essential are (1) that the opium residue before percolation be thoroughly dried, (2) that the acetone should not contain anything distilling below  $54^{\circ}\text{C}.$ , or above  $58^{\circ}\text{C}.$ , and (3) that after the added excess of iodine the container be continuously shaken until the precipitate is so fully separated that the solution above it is clear. An automatic shaker is an aid in this assay. A second estimation can be made with the remaining part of the lime solution.

Without the use of lime-water in purification of the morphine of the residue, we find the color of the resulting acidulous solution to be inconvenient in the titration, and find the percentage figure to be uniformly higher than when obtained after lime solution. The vessel is easily cleaned from adhering morphine periodide by the use of acetone.

#### RESULTS OF THE OPIUM ASSAY BY THE PERIODIDE METHOD.

We can give here the results of assays of but three samples of powdered opium, these coming from three different reputable houses. They were all marked, sample A to contain fourteen per cent., samples B and C to contain the quantity required by the U. S. P. Three analyses of each sample were made, and to sample A the U. S. P. method was also applied, and was found to contain 14.4 per cent. morphine by that method. The volumetric method was carried out exactly as described above.

##### SAMPLE A.

	Opium taken in grams.	Iodine consumed by one-half.	Percentage morphine found.
1.....	1.0036	0.116644	17.41
2.....	1.008	0.116732	17.37
3.....	1.0022	0.116642	17.44

##### SAMPLE B.

	Opium taken in grams.	Iodine consumed by one-half.	Percentage morphine found.
1.....	1.0033	0.08872	13.25
2.....	1.0023	0.08872	13.20
3.....	1.0026	0.08872	13.21

## SAMPLE C.

	Opium taken in grams.	Iodine consumed by one-half.	Percentage morphine found.
1.....	0.9969	0.096319	14.48
2.....	1.0016	0.097219	14.55
3.....	0.9988	0.094552	14.19

AS A VALUATION OF THE MORPHINE OF ANY PHARMACOPOEIAL  
ASSAY.

If it should be desired to estimate the alkaloid in the crystals obtained in assay by the pharmacopoeia of this or any other country, the periodide volumetric analysis could be well applied as follows :

Let the crude morphine obtained by the pharmacopoeial method be taken up with lime-water, the latter made up to a given volume, and a measured portion of the filtered solution, placed in a graduated vessel and acidulated with hydrochloric acid; let a definite excess of the decinormal iodine be added, in small portions at a time, and shaken after each addition, till the periodide separates out, and the clear liquid retains a dark red color, making up the mixture to a given volume, filtering off half and then titrating the excess of iodine in this half by standard sodium thiosulphate, the amount of iodine consumed can be easily found. Working on ten grams opium, a tenth portion of the lime-water solution would represent one gram of opium, and the percentage of morphine would be equal to the weight of iodine consumed, multiplied by 74.918, or to the number of cubic centimeters of the tenth-normal iodine consumed, multiplied by 0.94793. Several analyses could be made with the remaining part of the lime-water solution.

CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN,  
July, 1898.

## NEW BOOKS.

A LABORATORY GUIDE IN QUALITATIVE CHEMICAL ANALYSIS. BY H. L. WELLS, YALE UNIVERSITY. New York: John Wiley and Sons. pp. 189. Price \$1.50.

In the first nine chapters the author endeavors to get the student to learn, by direct experiment and by numerous questions, how to distinguish and divide what are usually termed bases

into the five or six generally accepted analytical groups. The purpose appears to be to make the student think, and there is little doubt but that if he conscientiously pursues the course outlined he will not fail to gain a very fair knowledge of the general principles of analysis.

Sixteen pages are devoted to the study of the acid radicals, the student being as before urged to test and note his discoveries. Numerous excellent practical hints appear here and there, helpful even to the more advanced student.

Two chapters are given to the analysis of solids and the preparation of reagents.

Part II considers theory. It discusses, among others, the radicals and formulas, ionizations and ions, etc. In the latter connection the author remarks, "the circumstance that ionization takes place greatly simplifies inorganic chemical analysis."

About a dozen pages are devoted to sensible and helpful suggestions on equation writing.

Part III considers the descriptive portion, which in most texts dealing with analysis, receives first attention.

The author has aimed to lead the student into analysis without resorting to the mechanical habit, and in this book contributes much to obviate and keep out this evil. He accordingly deserves great credit for his effort. Earnest teachers, who believe in laying a good foundation in analysis, will appreciate it and give the little volume a hearty welcome.

EDGAR F. SMITH.

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### ERRATA.

In the August issue, page 557, line 9, for "ammonium bromoselenide" read "ammonium bromoselenate."

Page 567, line 10 from bottom, for "ammonium selenium bromoselenate" read "ammonium bromoselenate."

Page 578, line 8, for "forty" read "four."

## BOOKS RECEIVED.

Bulletin No. 74. 1. The Chinch-bug. 2. Earthworms a Source of Gapes in Poultry. Kentucky Agricultural Experiment Station of the State College of Kentucky, Lexington, Ky. 29 pp.

Bulletin No. 75. Commercial Fertilizers. Kentucky Agricultural Experiment Station of the State College of Kentucky, Lexington, Ky. 18 pp.

Foods and Food Adulterants. Investigations made under direction of H. W. Wiley, chief chemist, with the collaboration of K. P. McElroy, W. H. Krug, T. C. Trescott, W. D. Bigelow, and others. Part Ninth.—Cereals and Cereal Products. Bulletin No. 13, Division of Chemistry, U. S. Department of Agriculture, Washington, D. C. vii + 206 pp.

Composition of Maize (Indian corn). Including the Grain, Meal, Stalks, Pith, Fodder, and Cobs. Compiled chiefly from the Records of the Division of Chemistry, by H. W. Wiley. Bulletin No. 50, U. S. Department of Agriculture, Division of Chemistry, Washington, D. C. 31 pp.

Experiments with Sugar-beets in 1897. By Harvey W. Wiley. Bulletin No. 50. U. S. Department of Agriculture, Division of Chemistry, Washington, D. C. 165 pp., with two maps.

Special Report on the Beet-sugar Industry in the United States. U. S. Department of Agriculture, Washington, D. C. 240 pp. with two maps.

Second Part of the Tenth Annual Report of the Storrs Agricultural Experiment Station, 1897. 148 pp. Storrs Agricultural Experiment Station, Storrs, Conn.

Explosive Materials. The Phenomena and Theories of Explosion and the Classification, Constitution, and Preparation of Explosives. By Captain John P. Wisser. New York: D. Van Nostrand Co. 1898. vi + 160 pp. Price 50 cents.

Strawberries. By L. C. Corbett. Bulletin No. 52. West Virginia Agricultural Experiment Station, Morgantown, W. Va. March, 1898. 23 pp.

Proceedings of the American Philosophical Society held at Philadelphia for Promoting Useful Knowledge. Vol. xxxvii, No. 157. July, 1898. Philadelphia: The American Philosophical Society, 104 South Fifth Street. 174 pp.

Commercial Fertilizers. Special Bulletin. Second Edition. H. A. Huston, State Chemist, Purdue University, Lafayette, Ind. 8 pp. and table.

Lehrbuch der anorganischen Chemie. Von Prof. Dr. H. Erdmann in Halle. Mit 276 Abbildungen und vier Farbigen Tafeln. Braunschweig: Friedrich Viewig und Sohn. 1898. xxvi + 756 pp. Large 8vo. Flexible cloth. Price M. 18.

Elements of General Chemistry with Experiments. By John H. Long, M.S., Sc.D. Chicago: E. H. Colegrove. 1898. 408 pp. Price \$2.00.

# THE JOURNAL

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## AMERICAN CHEMICAL SOCIETY.

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### VOLUMETRIC APPARATUS.<sup>1</sup>

BY G. F. BARTON.

Received August 19, 1898.

THERE have been various ideas as to what volumetric apparatus should represent, and the subject has been carefully studied in Europe for several years. Several reports have been made by German chemical societies and by committees of the international congresses of applied chemistry which have been held in Brussels and Paris during recent years. The Imperial Bureau of Weights and Measures of Germany has taken up the matter, and has minutely defined the conditions under which it works in testing apparatus submitted for that purpose. A report which I have not seen was submitted at the congress held recently in Vienna.

The various ideas as to what volumetric apparatus should represent may all be brought under the following three types: Apparatus of the first type contains the named volume at the specified temperature; of the second, contains such a volume of water at the specified temperature, that if (disregarding the container) the water were cooled down to  $3.93^{\circ}\text{C.}$ , its volume would be the named volume; of the third, contains the same number of grams of pure water free from air when weighed in dry air at the specified temperature and 760 mm. pressure, as the number of cubic centimeters or grams marked upon them.

Table I shows the volume of water contained at the various specified temperatures by liter flasks of these three types, the

<sup>1</sup>Read at the Boston Meeting of the American Chemical Society, August, 1898.

TABLE I.

## THE CALCULATED CONTENTS OF LITER FLASKS OF VARIOUS TYPES.

In these calculations it is assumed that the density of the weights is 8.3, that the barometer stands at 760 mm., that the coefficient of cubical expansion of glass is 0.00025, and that 1000 cc. of pure water, free from air, weigh 1000 grams *in vacuo* at 3.93° C.

Type.	Specified temperatures. °C. = °F.	Volumes con- tained at the specified tem- peratures.	Weight in air of water to fill the flask at the specified tem- peratures.	Volume con- tained at 22° C.	Weight in air of water con- tained at 22° C.
I. Contain the named volume at the specified temperatures.....	3.93 4.0 15.0 15.5 15.555+ 16.666+ 17.5 20.0 22.0	1000.000 1000.000 1000.000 1000.000 1000.000 1000.000 1000.000 1000.000 1000.000	998.879 998.879 998.051 997.978 997.967 997.790 997.648 997.173 996.747	1000.452 1000.450 1000.175 1000.161 1000.161 1000.133 1000.113 1000.050 1000.000	997.197 997.195 996.921 996.909 996.907 996.879 996.858 996.796 996.747
II. Contain such a volume of water at the specified temperature that if the water (disregarding the container) were cooled down to 3.93° C. the volume of the water would be the named volume.	15.0 15.555+ 22.0	1000.872 1000.958 1002.206	998.921 998.923 998.945	1001.047 1001.119 1002.206	997.790 997.862 998.945
III. Contain the same number of grams of pure water, free from air, when weighed at the specified temperature as the number of cubic centimeters or grams named upon them .....	3.93 4.0 15.0 15.5 15.555+ 16.666+ 17.5 20.0 22.0	1001.122 1001.122 1001.953 1002.026 1002.037 1002.215 1002.357 1002.835 1003.264	1000.000 1000.000 1000.000 1000.000 1000.000 1000.000 1000.000 1000.000 1000.000	1001.575 1001.573 1002.128 1002.189 1002.199 1002.348 1002.470 1002.885 1003.264	998.316 998.314 998.868 998.928 998.938 999.087 999.209 999.622 1000.000

weight of water which they would contain at the specified temperature, the volume which they would contain when at 22° C., and the weight which they would contain at 22° C. In this table appear temperatures that have never got much, if any, beyond being proposed. 3.93° C. is the temperature at which a liter of water is assumed to weigh a kilo, when weighed in a vacuum; 4° C. is the temperature commonly taken as that of the greatest density of water; 15° C. is probably the temperature most commonly used; 15.5° C. is used as an approximate equivalent of 60° F.; 15.555+° C. is the true 60° F.; 16.666+° C. equals 62° F., commonly used in England; 17.5° C. is the temperature proposed by Mohr originally; 20° C. is the temperature adopted by the Physikalisch-Technische Reichsanstalt for polariscopic apparatus; and 22° C. is a temperature proposed and advocated by Oldberg before the U. S. Pharmaceutical Association but not adopted by them. Under the second type are inserted only the values for temperatures at which apparatus is actually for sale together with those for 22° C.

In discussing the merits of the different types No. II may be neglected, since it is only used to a limited extent, and the principle upon which it is based holds good only for water. The real contention is between types I and III, and it will be noted at 15° C., for instance, that the errors possible are very considerable if part of the apparatus used in an analysis is of one type and part of another. Suppose, for example, a solution is made up to one liter in a flask of the first type and then 100 cc. taken for a determination in a pipette of the third type. The result will be that an error of 1/500 of the whole amount will be introduced into the result. Other instances might be mentioned but this is certainly sufficient to show the necessity for agreement as to the type to be used. It should be stated also before leaving this point, that the German Bureau of Weights and Measures only receive, for testing, apparatus graduated for 15° C. and of type I and that the published opinions of those who have made a study of the subject are almost universally in favor of the same type.

In view of the above facts, Table II, showing the results of tests actually made upon a series of flasks representing at least five and possibly six German and American makers, is of inter-

est. In the first column the flasks are numbered for convenience in reference; in the second are shown the labels; in the third the number of the type inferred from the label; in the fourth the volume or weight actually contained, provided the inference of the type from the label is correct; in the fifth the type inferred from the actual contents found by experiment; and in the last, the volume or weight contained, provided the second inference of the type is correct, appears.

TABLE II.  
TESTS OF FLASKS FROM DIFFERENT MAKERS.

No.	Label on flasks.	Type inferred from label.	Volume or weight at marked tem- perature if type inferred from label is correct.	Type inferred from contents.	Volume or weight at marked tem- perature if type inferred from contents is correct.
1	500 ccm. E+ 15° C.	I	500.002 cc.	I	500.002 cc.
2	1000 Gr. 15° C.	III	1000.453 grams	III	1000.453 g'ms
3	1000 c.c. 60° F.	I	1002.149 cc.	III	1000.112 cc.
4	1000 c.c. 60° F.	I	1002.388 cc.	III	1000.350 cc.
5	1000 ccm. 15° C.	I	1002.309 cc.	III	1000.355 cc.
6	1000 cc 60° F.	I	1001.056 cc.	II	1000.098 cc.
7	1 liter 60° F.	I	1001.120 cc.	II	1000.162 cc.
8	1000 c.c. (No. temp.)	I	998.991 cc. (at 15° C.)	Unknown	
9	1000 c.c. 60° F.	I	1002.599 cc.	III	1000.561 cc.
10	1000 cc 15° C.	I	1000.017 cc.	I	1000.017 cc.

It will be seen that the labels on flasks 1, 2, and 10 are the only ones from which the type was correctly inferred, and that flask 2 showed a variation of over  $\pm 0.3$  of a gram from the supposed contents. This limit of variation, it should be mentioned, is the one adopted for liter flasks by the German Bureau of Weights and Measures, and can be easily attained in practice. Flask 8 may be called grossly inaccurate, as it is impossible to infer from the contents what type the manufacturer had in mind. No temperature for working is given upon it. The other six flasks are all wrongly or insufficiently marked for distinguishing the type to which they belong, and 4, 5, and 9 are not within the above-mentioned limits.

Aside from the type, the most important question to be settled would seem to be the temperature at which volumetric apparatus should be standard. It is assumed for the purposes of this discus-



sion that every one prefers ware graduated according to type I or, in other words, containing the named volume, as distinguished from the weight, at the specified temperature. We may then proceed to discuss the various figures given under this type in Table I.

The volumes and weights at 22° C. given in the sixth and seventh columns of this table, are supposed to be the volumes and weights contained at the most commonly occurring temperature of the average laboratory. This temperature was selected for two reasons: First, Kilgore, by "a long series of experiments," found that the average temperature of his laboratory during the working day was 21.8° C.; and secondly, it is approximately the temperature which has been found most comfortable for people not doing manual labor and located in rooms having artificial ventilation.

From the volumes given in the sixth column it will be seen that the errors incident to using apparatus, standard at the temperatures given, when it is at the ordinary temperature of a room, may amount to from 0.45 cc. per liter with that standard at 3.93° C., to nothing with that standard at 22° C., and furthermore that the error in the case of apparatus standard at 15° C., would amount to nearly two-tenths cc. per liter. It may be claimed that it is perfectly possible to use flasks at 15° C. and that in other apparatus, since it is commonly used for volumes below 100 cc., the error would not be appreciable. This view might perhaps be accepted if the temperature never went above 22° C., but many of us, particularly in commercial laboratories, have been obliged to use burettes and pipettes at temperatures as high as 30° C., with the result that this error becomes appreciable, while if the apparatus were standard at 22° C., the error in using it at 29° C. would be the same that now obtains in using apparatus standard at 15° C. when at 22° C.

Considering the different temperatures individually, it is found that 3.93° C. is the temperature at which the brass gallons furnished the different states by the U. S. Government are standard, but that neither this temperature nor 4° C. is in general use. The temperatures 15.5° C. and 60° F. are gradually going out of use in this country. 62° F. is a temperature which has little or no foothold outside of England and certainly

would be useless as a standard temperature in this country.  $17.5^{\circ}\text{C.}$ , the temperature originally proposed by Mohr, appears to be gaining some favor in this country for a general temperature, although apparatus standard at that is not regularly on the market as far as the writer knows.  $20^{\circ}\text{C.}$  does not appear to be used except for polariscopic apparatus.  $22^{\circ}\text{C.}$  would seem to be the most natural temperature for use in this country if it were not for the confusion which would arise from other standards being used in other countries. But this confusion already exists and can hardly become worse by an attempt to crystallize chemical usage in this country at the most convenient temperature. It would seem that if confusion in regard to this point were such an obvious disadvantage, that a practical uniformity of usage would have already resulted by general consent. Looking at the question from a national rather than an international point of view, it is difficult to see the advantage of using any temperature below the average or the most common one of our laboratories; and surely there can be no reason, from this point of view, for discarding  $15^{\circ}$  for  $17.5^{\circ}$ , or any other temperature below  $20^{\circ}\text{C.}$  Any line of reasoning which led to the adoption of  $15^{\circ}\text{C.}$ , or any other temperature above that of the greatest density of water, would seem to be still more favorable to  $22^{\circ}$  or a similar temperature.

In the writer's opinion, the most commonly occurring temperature represented by even centigrade degrees, rather than the average temperature of the laboratory, ought to be considered the best temperature for general use.

In order to secure uniformity and accuracy in using volumetric apparatus, there are three minor points which must certainly be taken into account. These are, the method of reading the meniscus, the rapidity with which delivery takes place in a burette or pipette, and the time allowed for draining in using apparatus graduated to deliver rather than to contain.

There seems to be a practical agreement in reading the extreme bottom of the meniscus, but in the times of delivery and of draining, anything but uniformity prevails. The German Bureau of Weights and Measures have a standard practice in regard to all three of these points, an account of which they have published, together with other regulations in regard to

graduated ware tested by them. A translation by Mr. E. E. Ewell, of this article, is to be found in an appendix to the "Proceedings of the Fourteenth Annual Convention of the Association of Official Agricultural Chemists." The original reference is *Zeitschrift für angewandte Chemie*, 1893, pp. 557-559.

For the sake of showing the probable errors in checking graduated glassware, Table III, giving the results of ten determinations of the contents of the same liter flask, together with the probable error in any one observation, and the probable error in the mean, is introduced.

TABLE III.  
DUPLICATE TESTS OF FLASK NO. 3.

Experiment No.	Contents in cubic centimeters at the specified temperature.
2	1002.108
8	1002.110
4	1002.118
9	1002.129
5	1002.133
7	1002.163
10	1002.164
3	1002.174
6	1002.183
1	1002.206

Probable error of any one observation  $\pm 0.0228$ .

Mean 1002.149

Probable error of Mean  $\pm 0.0072$ .

The method used in these determinations, as well as in those of Table II, was to weigh the flask, fill it with boiled distilled water, and allow it to remain near the balance-case until the temperatures of the air and water were within  $1^{\circ}$  C. of each other. Then water was removed until the proper reading was obtained and the flask introduced into the balance and weighed by the method of Gauss. On removing the flask from the balance-case, the reading was checked to show that no appreciable expansion of the water had taken place, and the temperature of the water noted. The dry and wet bulb thermometers, the barometer and its thermometer, were also read. From the data thus obtained the values given in Tables II and III were calculated.

The most important source of error in this work was found to

be in taking the temperature of the water, for a variation of  $0.1^{\circ}$  C. made a difference in the final contents of the flask of approximately 0.02 cc. The thermometer used in the work was thoroughly tested and found to be correct within  $0.1^{\circ}$  C.

The variations in the buoyant effect of the air, due to variations in the barometer, were also taken into account, but it required a variation of fifteen mm. in the corrected reading to produce the same effect upon the weight of a liter of water that was produced by  $0.1^{\circ}$  in temperature. The barometer readings were not corrected for variation of the latitude from  $45^{\circ}$ , which, as the latitude was approximately  $40^{\circ}$ , would have introduced a correction of  $-0.35$  for 760 mm. ; or for elevation above the sea-level, which as it was only about twenty-five meters, would have introduced a correction of  $-0.004$  mm. Corrections for tension of aqueous vapor and temperature were, however, introduced, the values given in "Smithsonian Meteorological Tables" for 1896 being used.

The coefficient of cubical expansion of glass was assumed to be 0.000025. The very improbable error of two in the second significant figure of this number, would amount to only 0.014 of a gram in the final weight of a liter of water under average conditions.

The density of the weights was assumed to be eight and three-tenths, and it was found that an error here of one-tenth would result in an error of approximately 0.0017 of a gram in the final weight of the water.

The buoyant effect of the air upon the weight of the flask was assumed to be a constant.

The table giving the density of water at various temperatures was furnished by the Office of Standard Weights and Measures, at Washington, and is the one used by them. The values are those determined by M. P. Chappuis and published by the International Bureau of Weights and Measures in "Procès-Verbaux des Seances" for 1892. The table giving the weight of a liter of air at various temperatures, was furnished by the same office. It was computed by Dr. O. J. Broch, from Regnault's observations, and published in Vol. I of "Travaux et Memoires du Bureau International des Poids et Mesures." It was found that by using different data for the densities of water and the

weight of a liter of air or by using some of the published tables for obtaining the weight of a volume of water at different temperatures, an error of two-tenths of a gram might be introduced into the calculated weight of a liter.

The weights used had been compared with a standard set, originally tested and furnished with a table of corrections by the U. S. Office of Standard Weights and Measures, so that all weights were in terms of the International kilogram.

The balance was made especially for this kind of work, with large bows and pans. A variation of one division in the rest-point corresponded to six milligrams with a load of 1200 grams in each pan.

It remains for us to consider how the individual members of this society may advance the cause of uniformity in volumetric apparatus. There are two parties to be kept in mind, who look at this matter from entirely different points of view; namely, the manufacturer and the consumer. The manufacturer can be influenced only by the demands of his customers. If any considerable number of them ask for one thing, although he may decline the first few orders, the constant dropping will finally wear away the stone, and the article asked for will be added to his regular stock list.

Therefore, it must remain for us as individual customers, after committees, etc., have furnished the necessary information, to produce uniformity in the graduation and use of volumetric apparatus by instituting an overwhelming demand for the proper kind.

LABORATORY AND GRADUATING DEPARTMENT  
OF WHITTALL, TATUM & CO., August, 1898.

## THE ALKALINE REACTION OF SOME NATURAL SILICATES.<sup>1</sup>

BY F. W. CLARKE.

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THAT pure water exerts a distinct solvent action upon many natural silicates has long been known. As far back as 1848 the Rogers brothers published a series of observations upon this subject,<sup>2</sup> and showed that some species of minerals would

<sup>1</sup> Read at the Boston meeting of the American Chemical Society, August, 1898.

<sup>2</sup> *Am. J. Sci.* (2), 5, 401.

give an alkaline reaction to test paper. They did not, however, give details concerning the individual minerals thus investigated. The more recent researches of Daubrée and of Cossa are well known.

By the use of phenolphthalein as an indicator the alkalinity of many silicates can be demonstrated with the utmost ease, and the experiments described below serve to bring out very clearly the relative decomposability of certain minerals and rocks by pure water. The method adopted was as follows: A series of glass-stoppered bottles was placed against a white background. In each bottle half a gram of finely pulverized mineral was put, and then fifty cc. of distilled water, containing a very little alcoholic phenolphthalein, was added. As the indicator was mixed, once for all, with the total amount of water taken for the entire series, the twenty-two samples examined were treated exactly alike. Two of the bottles were filled with the water and indicator in blank, in order that possible action upon the glass itself might be detected if it occurred. The two blanks, however, remained colorless during the two weeks through which the experiments lasted. The results obtained were as follows:

*Muscovite*.—A doubtful trace of coloration, which soon disappeared.

*Lepidolite*.—Like muscovite.

*Phlogopite*.—The peculiar non-fluoriferous variety from Edwards, N. Y. Gave a very distinct, permanent, pink coloration.

*Orthoclase*.—A trace of coloration which increased for a few days and then faded.

*Oligoclase*.—The transparent variety from Bakersville, N. C. Distinct and permanent, but pale coloration.

*Albite*.—From Amelia County, Va. Gave a good, permanent, alkaline reaction.

*Leucite*.—A slight reaction at first, which faded in a few days.

*Nephelite*.—The elaeolite from Litchfield, Maine. Good coloration, but partly fading in time.

*Cancrinite*.—Litchfield, Maine. Gives a deep rose coloration, which is permanent.

*Sodalite*.—From Canada. A deep, permanent rose color.

*Spodumene*.—The transparent, yellow variety from Brazil. A good reaction, but gradually fading.

*Scapolite*.—The wernerite from St. Lawrence County, N. Y. Gave a faint, evanescent trace of coloration.

*Laumontite*.—A doubtful trace of coloration.

*Stilbite*.—Faint, evanescent coloration.

*Chabasite*.—Like stilbite.

*Heulandite*.—Slight reaction, but distinct.

*Thomsonite*.—Variety lintonite. A fairly strong reaction, fading in time.

*Analcite*.—Good alkaline reaction.

*Natrolite*.—From Bohemia. Strong coloration, permanent.

*Pectolite*.—From Bergen Hill. Gave a very deep rose color.

*Apophyllite*.—From Bergen Hill. A very deep rose color.

In nearly every case the reaction was obtained at once, showing a more rapid action of water upon the silicate than had been anticipated. In some instances fading is noted. This is doubtless due, in general, to the action of light; but in certain cases the colored solution separated into two layers, the color being wholly in the lower. Here the color was really held as a coating upon the fine solid particles, and as they subsided the appearance of stratification was produced. Towards the end of the experiments the mineral aegirite was added to the series. This also gave a strong alkaline reaction and a fairly deep rose color.

A neat method of demonstrating the reactions described above is the following: Place a little of the mineral to be tested in a watch-glass upon a sheet of white paper. Add a drop of alcoholic phenolphthalein solution, and then a few drops of pure water; in most cases the reaction is given instantaneously. Orthoclase gave no coloration, leucite a trace, and scapolite a trace; albite, nephelite, and phlogopite furnished distinct reactions. Under the same circumstances thomsonite, aegirite, natrolite, cancrinite, sodalite, pectolite, and apophyllite gave immediately a deep, rich, rose color. The strongest alkaline reactions seemed to be given by pectolite and apophyllite.

In general, the order of intensity of the color produced was what might have been expected. Among the micas, muscovite and lepidolite showed little or no solubility, while phlogopite

was distinctly attacked. In nature the magnesian micas are far more easily alterable than muscovite, a fact which is reiterated by these experiments. Again, orthoclase was slightly dissolved, albite much more so, and oligoclase gave a reaction between the two; that is, more than the one, less than the other. In other words, the plagioclase feldspars alter more easily than orthoclase, as is apparent in the study of the rocks themselves.

In order to bring out the latter point more clearly, a series of rocks which had been analyzed in the laboratory of the U. S. Geological Survey, was placed in a row of bottles, and treated just as the mineral species had been, with water and phenolphthalein. A granite and an amphibole gabbro gave no alkaline reaction. A rhyolite, trachyte, leucite basalt, feldspar basalt, and diorite gave faint traces of color. Granitite, gneiss, phonolite, diabase, and camptonite yielded distinct alkaline colorations.

In all of these instances the production of color is doubtless due to the solution from the mineral or rock of alkaline silicates. The noteworthy point is the quickness with which the reaction can be obtained. With minerals like cancrinite, sodalite, natrolite, pectolite, and apophyllite, the reaction is striking enough to be used as a lecture-table experiment.

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[CONTRIBUTION FROM THE LABORATORIES OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

## THE SOLUBILITY OF SALTS OF WEAK ACIDS IN STRONGER ACIDS.<sup>1</sup>

BY ARTHUR A. NOYES AND DAVID SCHWARTZ.

Received August 20, 1898.

### I. PURPOSE OF THE INVESTIGATION.

THE theory of the influence of one electrolyte on the solubility of another whose ions differ from those of the first, has up to this time, in spite of the practical importance of the question, been developed and tested only in a very incomplete way. A few years ago, to be sure, the influence on the solubility of a strongly dissociated salt by another of approximately the same dissociation was calculated by one of us,<sup>2</sup> and was experimentally determined in the case of thallium chloride in

<sup>1</sup> Read at the Boston Meeting of the American Chemical Society, August, 1898.

<sup>2</sup> *Ztschr. phys. Chem.*, 6, 262.



the presence of potassium nitrate and sodium acetate, an approximate agreement being found to exist. A case of greater importance, however, is that in which a weakly dissociated substance is formed by the reaction, such as takes place in the action of a strong acid on the salt of a weaker acid; for in that case the change in solubility is very great. The purpose of this article is to derive theoretically the equations applicable to this case, and to present the results of an experimental investigation of the correctness of these equations. We have accordingly determined the solubility of silver benzoate in nitric acid, a very strong acid, and in chloracetic acid, a comparatively weak one at different concentrations, and compared the observed with the theoretical values. We will first describe the method of carrying out the experiments and then present the results.

## 2. DESCRIPTION OF THE EXPERIMENTS.

The silver benzoate was prepared by adding to an excess of commercial benzoic acid a solution of sodium carbonate, boiling until the solution was freed from carbon dioxide, and then treating the solution with silver nitrate. The precipitate thus obtained was washed with water and crystallized twice out of boiling water. Its purity was established by ignition and weighing the resulting silver; the amount found agreed with that calculated in two determinations within two-tenths milligram.

The nitric acid solution was prepared from a commercial chemically pure acid which was free from chlorine and which on evaporation left only an inappreciable residue. The chloracetic acid consisted of that portion of a commercial sample which boiled between  $185^{\circ}$  and  $186^{\circ}$ . The strengths of these solutions were determined with a sodium hydroxide solution which had been titrated against a sample of succinic acid, the purity of the latter having been proved by a measurement of its electrical conductivity.

The saturation of the solutions was effected by rotation in the previously described apparatus<sup>1</sup> at a temperature of  $25^{\circ}$ . In each case the determinations were made in pairs, so that the condition of saturation was approached from a higher as well as

<sup>1</sup> *Ztschr. phys. Chem.*, 9, 603.

from a lower temperature. After a rotation of at least eight hours, the solutions were filtered, since they would not completely settle; and a portion of 100 cc. was at once measured out with a pipette and titrated with a twentieth-normal solution of potassium thiocyanate with the addition of nitric acid and ferric alum as indicator.

### 3. THE EXPERIMENTAL RESULTS.

The following tables contain the results of all the solubility determinations. The numbers express the millimols of silver benzoate dissolved in one liter. The values which were obtained by cooling the solutions to 25° are placed under the heading "supersaturated," while those obtained by heating to 25° are designated as "undersaturated."

#### SOLUBILITY OF SILVER BENZOATE IN PURE WATER.

Undersaturated.	Supersaturated.	Undersaturated.	Supersaturated.
11.40	12.04	11.61 <sup>1</sup>	11.68
11.43	12.44	11.61 <sup>1</sup>	11.62
11.43	12.74	11.63 <sup>1</sup>	11.66
11.49	12.27	11.46	11.97
11.47	12.14	12.14 <sup>2</sup>	12.35
11.42	12.24	11.45	13.86 <sup>3</sup>
11.42	11.96	11.40	12.86
....	....	11.43	12.92

Mean of the undersaturated solutions:  $11.47 \pm 0.017$  or  $11.44 \pm 0.007$ .

Mean of the supersaturated solutions:  $12.21 \pm 0.091$ .

#### SOLUBILITY OF SILVER BENZOATE IN NITRIC ACID.

Concentration of acid. 4.435 millimols per liter.		Concentration of acid. 8.870 millimols per liter.		Concentration of acid. 8.915 millimols per liter.	
Under- saturated.	Super- saturated.	Under- saturated.	Super- saturated.	Under- saturated.	Super- saturated.
13.97	14.75	17.00	17.34	17.15	17.57
13.92	15.07	16.96	18.20	17.15	18.07
13.95	14.87	17.19	17.11	....	....
13.94	14.86	16.75	17.64	....	....
14.21 <sup>1</sup>	14.16 <sup>1</sup>	....	....	....	....
13.95	14.62	....	....	....	....
13.95	14.83	16.98	17.57	17.15	17.82
$\pm 0.006$	$\pm 0.054$	$\pm 0.060$	$\pm 0.174$	$\pm 0.000$	$\pm 0.179$

<sup>1</sup> Omitted in the calculation of the second mean.

<sup>2</sup> Omitted in the calculation of both means.

<sup>3</sup> Omitted in the calculation of the mean.

Concentration of acid. 17.74 millimols per liter.		Concentration of acid. 17.83 millimols per liter.		Concentration of acid. 26.74 millimols per liter.	
Under-saturated.	Super-saturated.	Under-saturated.	Super-saturated.	Under-saturated.	Super-saturated.
23.27	24.07	23.47	24.83	30.70	31.10
23.23	24.21	23.55	24.97	30.68	35.12
23.46 <sup>1</sup>	23.93	....	....	30.77	31.93
23.21	23.97	....	....	30.67	33.30
23.24	24.05	23.51	24.90	30.71	32.86
±0.013	±0.048	±0.029	±0.050	±0.016	±0.674

## SOLUBILITY OF SILVER BENZOATE IN CHLORACETIC ACID.

Concentration of acid. 3.935 millimols per liter.		Concentration of acid. 7.87 millimols per liter.		Concentration of acid. 15.74 millimols per liter.	
Under-saturated.	Super-saturated.	Under-saturated.	Super-saturated.	Under-saturated.	Super-saturated.
13.86	13.86	16.10	16.18	20.92	21.13
13.81	14.29	16.10	16.36	20.94	25.09 <sup>1</sup>
13.86	14.16	16.12	16.56	20.90	21.40
13.86	14.16	16.14	16.38	20.95	21.09
13.85	14.12	16.12	16.37	20.93	21.21
±0.019	±0.064	±0.008	±0.050	±0.010	±0.076

The relatively large number of solubility determinations in pure water were carried out because the supersaturated and the undersaturated solutions did not correspond. The seven pairs of values in the first two columns were obtained after six hours' rotation of the solutions; the first five in the third and fourth columns, after twenty-four hours; and the last three in these columns, after seventy-two hours. The saturation seems, however, to depend much more on the quantity and physical condition of the solid substance than on the time. As is seen, the mean of the supersaturated solutions is six and four-tenths per cent. higher than that of the undersaturated. From the fact, however, that the separate undersaturated values agree well with one another, while the supersaturated ones show large variations, the former may be considered as essentially correct. In the two cases, the average deviations of the means amount to 0.15 and 0.75 per cent. respectively, and if these values were combined according to the laws of probability, then a relative weight of only four per cent. would have to be ascribed to the supersaturated. Paul<sup>2</sup> had exactly the same experience in his researches on the solubility of certain organic acids whose phys-

<sup>1</sup> Omitted in the calculation of the mean.

<sup>2</sup> *Ztschr. phys. Chem.*, 14, 112.

ical condition is similar to that of silver benzoate. He also came to the conclusion that the undersaturated values are the reliable ones. The same difference between the results of the two methods of determination also exists in the presence of the two acids. We have therefore taken the mean value of the undersaturated solutions as the more reliable. These will be brought together in a table below.

#### 4. THE THEORY OF SOLUBILITY EFFECT.

We will now determine whether the experimental values are in accordance with the requirements of the theory of solubility effect. In order to do this, it is necessary to derive from the laws of mass-action the equations which should express the relation between the solubility of the silver benzoate in pure water and its solubility in the solutions of nitric acid and of chloroacetic acid. This we will now proceed to do in a general form.

The problem is the determination of the solubility of a di-ionic electrolyte AB in a solution which contains a known amount of a second di-ionic electrolyte CD. (An influence on the solubility takes place, since by metathesis certain amounts of the substances AD and CB are produced.) The solubility of the body AB in pure water and the dissociation relations of all the substances involved are to be assumed to be known.

First it is to be noticed that the following eight substances are present in the solution: the four undissociated substances AB, CD, AD, and CB; and the four ions, A, B, C, and D. We will designate the concentrations of the ions by these same large letters, and those of the undissociated molecules AB, CD, AD, and CB by the small letters  $a$ ,  $b$ ,  $c$ , and  $d$  respectively. If now the solution contains the known amount  $n$  of the substance CD in one liter, and the solubility in it of the substance AB is  $m$ , evidently the following equations hold true:

$$a + c + A = m, \quad (1)$$

$$a + d + B = m, \quad (2)$$

$$b + c + D = n, \quad (3)$$

$$b + d + C = n. \quad (4)$$

Further if  $m_0$  is the solubility of AB in pure water, and  $\alpha_0$  is

the corresponding dissociation, we obtain as the expression of the solubility principles: <sup>1</sup>

$$a = m_0(1 - a_0). \quad (5)$$

$$A \times B = m_0^2 a_0^2 = k_a, \quad (6)$$

where  $k_a$  is used for brevity to express the product  $m_0^2 a_0^2$ . Finally the following three dissociation equations apply:

$$\frac{C \times D}{b} = k_b, \quad (7)$$

$$\frac{A \times D}{c} = k_c, \quad (8)$$

and 
$$\frac{C \times B}{d} = k_d, \quad (9)$$

where  $k_b$ ,  $k_c$ , and  $k_d$  are the dissociation constants of the substances CD, AD, and CB respectively.

We now have nine equations and nine unknown quantities; namely, the concentrations of the eight different kinds of molecules and the value  $m$ . Theoretically then this latter quantity can be determined and we have convinced ourselves that the necessary eliminations can be carried out; that is to say, an equation can be obtained which contains as an unknown quantity only the quantity  $m$ , but the equation is of a high degree in  $m$  and consists of a very large number (probably a hundred or more) of terms. Accordingly the calculation has not been carried out, especially since this most general case finds no practical application, because at least one of the substances CD, AD, and CB must be a salt to which the theoretical laws of dissociation do not apply.

There is a possibility of simplifying the problem since a sufficiently accurate knowledge of one or two of the three values  $b$ ,  $c$ , and  $d$  can be obtained from other sources, whereby the corresponding dissociation equations can be dispensed with in the elimination, and the algebraic solution becomes much simpler. For, the dissociation of a substance in pure water can always be determined by means of conductivity measurements, and in the case of a largely dissociated substance, like a salt, or a strong acid or base in dilute solution, its disso-

<sup>1</sup> *Ztschr. phys. Chem.*, 4, 372; 9, 603.

ciation is influenced so little by the presence of other substances that its undissociated amount can be quite accurately estimated by a short approximation process. Since now at least one of the three bodies CD, AD, and CB must be a salt, it is always possible to simplify in this manner.

The simplest cases are those in which all three of the substances CD, AD, and CB, or the last two of these, are strongly dissociated substances, so that the quantities  $b$ ,  $c$ , and  $d$ , or the last two of them, can be determined from the conductivities of the salts in pure water. The solubility of thallium chloride in potassium nitrate, referred to at the beginning of this article, is one example of this kind. That of silver benzoate in sodium nitrate would be another. This case, is not, however, of present interest, as we have no new experiments of the kind to communicate.<sup>1</sup>

The next simplest case is that where CD and AD (or CB) are strongly dissociating substances, while CB (or AD) is only slightly or moderately dissociated. In this case the quantities  $b$  and  $c$  (or  $d$ ) can be determined from conductivity measurements, and can therefore be regarded as known quantities in the derivation of the final equation, so that equations (7) and (8) (or (9)), which contain them, can be dispensed with. The solubility of the silver benzoate in nitric acid is a case of this kind; for nitric acid and silver nitrate are strongly dissociated, and benzoic acid is weakly dissociated.

In order, now, to derive this equation, we assume  $b$  and  $c$  to be known, so as to have a definite case under consideration, and proceed as follows: For brevity we put

$$m - a = x, \quad (10)$$

$$\text{and} \quad n - b = l, \quad (11)$$

$l$  being a known quantity, and  $x$  the quantity to be determined. By elimination between equations (1), (2), and (6), we obtain:

$$d = \frac{x^2 - cx - k_a}{x - c}.$$

Furthermore we obtain by combining equations (2), (4) and (9):  $d = \frac{1}{2}(x + l + k_a \pm \sqrt{x^2 + l^2 + k_a^2 + 2xk_a + 2lk_a - 2lx})$ .

<sup>1</sup> For a full discussion of the theory in this case see Noyes: *Ztschr. phys. Chem.*, 27.

If now we place these two values of  $d$  equal to each other and simplify, we obtain the following expression :

$$x^3 + (r - 2c)x^2 + (c^2 - rc - rn + rb - k_a)x + (rcn - rc b + k_a c - k_a r) = 0, \quad (12)$$

in which  $r = \frac{k_a}{k_d}$ . By means of this equation we can calculate the value of  $x$ , since all the other values are known, and from this we obtain the solubility  $m$  by equation (10). In the case where the substance AB is difficultly soluble and the value  $n$  is not very great, the quantities  $b$  and  $c$  are negligible. Then the following equation applies :

$$x^3 + rx^2 - (rn + k_a)x - k_a r = 0. \quad (13)$$

If further  $x$  is very small relatively to  $r$ , the cubic term may be neglected. In this case :

$$x^2 - (n + k_d)x - k_a = 0. \quad (14)$$

The remaining case to be considered is that where only the substance AD (or CB) is strongly dissociated, both CD and CB (or AD) being only slightly or moderately dissociated, so that they follow the theoretical dissociation-law. In this case only the quantity  $c$  (or  $d$ ) can be regarded as known, and only equation (8) (or (9)) can be dispensed with in the derivation of the solubility equation. For the sake of definiteness we assume  $c$  to be known.

The solubility of silver benzoate in chloracetic acid is an example of this case, for chloracetic acid and the benzoic acid produced by the metathesis are weakly dissociated, and the silver chloracetate is much dissociated.

To derive the solubility equation, equations (3), (4), and (7) are solved for  $b$  with elimination of C and D, whereby we obtain :

$$2b = -(c + d - 2n - k_b) \pm \sqrt{(c + d - 2n - k_b)^2 + 4(cn + dn - n^2 - cd)}.$$

Eliminating B and C from equations (2), (4), and (9), we obtain :

$$2b = \frac{2(n - d)(x - d) - 2k_d d}{(x - d)}.$$

If now we place these values of  $2b$  equal to each other, simplify, and substitute in the resulting equation the value of  $d$  derived from equations (1), (2), and (6), *viz.*,  $d = \frac{x^2 - cx - k_a}{x - c}$ , after simplification we obtain :

$$rx^3 + (1 - 3cr)x^2 + (3c^2r - 3c + k_b - 2k_d)x^2 + (4ck_d - c^2r + 3c^2 - 2k_a - 2ck_b + s)x^2 + (k_ak_d - 2c^2k_d + 3ck_a - c^2 - k_ak_b + c^2k_b - ns - cs)x + (k_a^2 - ck_ak_d - c^2k_a + ck_ak_b + cns - k_as) = 0, \quad (15)$$

in which  $x = m - a$ ;  $r = \frac{k_d}{k_a}$ ; and  $s = \frac{k_b k_b}{k_a}$ . In very dilute solutions, or in general as an approximation,  $c$  may be placed equal to 0, when follows :

$$rx^3 + x^2 + (k_b - 2k_d)x^2 + (s - 2k_a)x^2 + (k_ak_d - k_ak_b - ns)x + (k_a^2 - k_as) = 0. \quad (16)$$

In certain cases, for example, when  $k_b$  is negligible in comparison with  $k_a$ , or the reverse, a further simplification may easily be made.

#### COMPARISON OF THE EXPERIMENTAL AND THEORETICAL VALUES.

We have, now, by means of equation (12), calculated the theoretical solubility of silver benzoate in the various solutions of nitric acid, making use of the following data :  $k_a = m_0 a_0 = 0.0000932$  (since the solubility in pure water,  $m_0 = 0.01144$ , and the corresponding dissociation-value,  $a_0 = 0.844$ , according to conductivity measurements of our own) ; the dissociation constant of benzoic acid,  $k_d = 0.000060$ , according to Ostwald's measurements, whence the ratio  $r = 1.553$ . The values of  $c$  in the different cases were deduced from the conductivity of silver nitrate as determined by Kohlrausch. The equations were solved in this case and also in that of the chloracetic acid, by repeated substitution of estimated values of  $x$  until the exact root was found.<sup>1</sup>

The solubility of silver benzoate in chloracetic acid has been calculated by equation (15), using the same values of  $k_a$  and  $k_d$ , as before, putting the dissociation constant of chloracetic acid,

<sup>1</sup> For further details of the method of calculation, reference is made to a more extended article on the theory in the current volume of the *Zeitschrift für physikalische Chemie*.



$k' = 0.00155$ , in accordance with the measurements of Ostwald, and determining  $c$  from conductivity measurements.

In the following tables are given the experimental and the theoretical values, together with the percentage differences between them.

SOLUBILITY OF THE SILVER BENZOATE IN NITRIC ACID.

Experiment No.	Concentration of the nitric acid.	Found solubility.	Calculated solubility.	Percentage difference.
I	0.00	0.01144	.....	.....
II	0.004435	0.01395	0.01406	+0.78
III	0.008870	0.01698	0.01703	+0.29
IV	0.008915	0.01715	0.01706	-0.53
V	0.01774	0.02324	0.02390	+2.76
VI	0.01783	0.02351	0.02396	+1.89
VII	0.02674	0.03071	0.03159	+2.79

SOLUBILITY OF THE SILVER BENZOATE IN CHLORACETIC ACID.

Experiment No.	Concentration of the chloracetic acid.	Found solubility.	Calculated solubility.	Percentage difference.
I	0.00	0.01144	.....	.....
II	0.003935	0.01385	0.01368	-1.24
III	0.00785	0.01612	0.01588	-1.51
IV	0.01574	0.02093	0.02117	+1.13

The agreement between the found and the calculated values is very satisfactory, especially considering the large number of dissociation values used in the calculation; consequently the solubility principles and the validity of the theoretical laws of dissociation in the case of weakly dissociated acids are again confirmed. It is specifically shown by this investigation that the solubility of silver benzoate is increased both by nitric acid and chloracetic acid in such a way that the product of the concentrations of the Ag and the  $C_6H_5CO_2$  ions remains constant.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORIES OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

THE SOLUBILITY OF ACIDS IN SOLUTIONS OF THE SALTS OF OTHER ACIDS.<sup>1</sup>

BY ARTHUR A. NOYES AND EDWARD S. CHAPIN.

Received August 29, 1898.

I. PURPOSE OF THE INVESTIGATION.

**I**N an article published elsewhere by one of us,<sup>2</sup> the theory of the influence of one di-ionic electrolyte on the solubility of

<sup>1</sup> Read at the Boston meeting of the American Chemical Society, August, 1898.

<sup>2</sup> *Ztschr. phys. Chem.*, 27.

another with different ions, was developed for the different cases actually occurring. Certain experiments made with the object of testing the theoretical equations so derived have been presented in the preceding paper; but there remains an especially important case to which the application of the theory has not yet been experimentally tested,—that involving the effect of a neutral salt of a partially dissociated acid on the solubility of another acid, likewise only partially dissociated. An example of this kind would be the effect of sodium acetate or of sodium formate on the solubility of benzoic acid, and we have in fact investigated this case, using each of the salts at different concentrations.

## 2. DESCRIPTION OF THE EXPERIMENTS.

In the first place the preparation of the substances and of the solutions employed will be described. The benzoic acid was prepared from a commercial sample by dissolving in the sodium carbonate solution, *partially* precipitating with dilute hydrochloric acid, and twice recrystallizing from boiling-water. As powdered benzoic acid probably saturates a solution much more quickly than does the crystallized form, the acid was then melted and finely pulverized. It was shown by qualitative test to be free from chlorine.

The sodium acetate and sodium formate used were prepared by twice recrystallizing the commercial salts. Solutions of these were made up by weighing out roughly the air-dried salts; and their concentrations were then accurately determined by evaporating measured portions with hydrochloric acid in platinum dishes, moistening the residue with the acid, and igniting gently until a constant weight was obtained. The three check determinations made in each case agreed within three-tenths per cent.

The solubility determinations were made by rotating for about sixteen hours at 25° in the previously described apparatus<sup>1</sup> bottles containing pure water or the solutions of sodium acetate or sodium formate and an excess of the solid benzoic acid. In one-half of the experiments the state of saturation was approached by cooling the solutions from a higher temperature,

<sup>1</sup> *Ztschr. phys. Chem.*, 9, 606.

and in the other half by warming from a lower temperature. Portions of the solution were quickly filtered, and twenty-five cc. measured out with a pipette and titrated, using phenolphthalein as an indicator, with a barium hydroxide solution which had been standardized by means of calcium carbonate and succinic acid, and which was 0.02936 normal.

### 3. THE EXPERIMENTAL RESULTS.

The following tables contain the results of all the solubility experiments. The numbers express the quantity of dissolved benzoic acid in millimols per liter. Those values which were obtained by cooling the solutions down to 25° are placed under the heading "supersaturated;" while those obtained by heating up to 25° are designated as "undersaturated."

#### SOLUBILITY OF BENZOIC ACID IN PURE WATER.

No.	Supersaturated.	Undersaturated.
1	27.92	28.02
2	27.80	27.79
3	28.10	27.88
4	28.22	27.80
5	27.96	27.81
Mean	28.00	27.86
	±0.058	±0.032

#### SOLUBILITY OF BENZOIC ACID IN SODIUM ACETATE SOLUTIONS.

Experiment number.	Concentration of the salt. 13.21 millimols.		Concentration of the salt. 26.41 millimols.		Concentration of the salt. 52.82 millimols.	
	Super-saturated.	Under-saturated.	Super-saturated.	Under-saturated.	Super-saturated.	Under-saturated.
1 ....	38.84	38.71	48.55	48.32	64.92	64.58
2 ....	....	....	48.44	48.28	64.90	64.70
Mean..	38.84	38.71	48.50	48.30	64.91	64.64

#### SOLUBILITY OF BENZOIC ACID IN SODIUM FORMATE SOLUTIONS.

Experiment number.	Concentration of the salt. 14.14 millimols.		Concentration of the salt. 28.28 millimols.		Concentration of the salt. 56.57 millimols.	
	Super-saturated.	Under-saturated.	Super-saturated.	Under-saturated.	Super-saturated.	Under-saturated.
1 ....	34.65	34.65	38.85	38.83	45.36	45.24
2 ....	34.52	34.42	39.00	38.84	45.33	45.27
Mean..	34.59	34.54	38.93	38.84	45.35	45.26

It will be seen from an examination of the tables that the supersaturated values are, in general, from three-tenths to five-tenths per cent. higher than the undersaturated values, a result which may be regarded as very satisfactory, in view of the diffi-

culty in this respect often experienced in solubility 'experiments with organic substances.'<sup>1</sup> In the subsequent calculations and summary of results, the averages of the supersaturated and undersaturated mean values are adopted as most probably correct.

#### 4. COMPARISON OF THE EXPERIMENTAL WITH THE CALCULATED VALUES.

It remains now to determine to what extent the values found as above described agree with the requirements of the theory of solubility effect. In order to determine this, we have calculated the solubility of the benzoic acid in the various salt solutions from its solubility in pure water and the dissociation relations of the substances involved, using the equation applicable to this case, derived in the preceding article of Noyes and Schwartz. This equation is

$$x^3 + (r - 2c)x^2 + (c^2 - rc - rn + rb - k_a)x + (rcn - rcb + k_ac - k_ar) = 0,$$

in which

$$x = m - m_o(1 - a_o) \text{ and } k_a = m_o^2 a_o^2,$$

where  $m_o$  and  $m$  are the solubilities of the benzoic acid in pure water and in the salt solution of the concentration  $n$ , and where  $a_o$  is the dissociation corresponding to the concentration  $m_o$ ; in which, further,  $r = \frac{k_a}{k_d}$ , where  $k_d$  is the dissociation-constant of the acetic or formic acid; and in which  $b$  and  $c$  represent the undissociated portions of sodium acetate or formate and of sodium benzoate respectively.

The data in the calculations by this formula are the following: The solubility in pure water  $m_o$  was found by our experiments to be 0.02793; the dissociation  $a_o$  corresponding to this was calculated from the dissociation constant 0.060, determined by Ostwald, and found to be 0.0453, from which it follows that  $k_a = 0.001601$ . The dissociation constants  $k_d$  of acetic and formic acids are respectively 0.0018 and 0.00214. The values of  $b$  and  $c$  varied in the different cases and were determined as described in the article just referred to from the electrical con-

<sup>1</sup> Compare Paul: *Ztschr. phys. Chem.*, 24, 112, and the preceding article.

ductivity of the salts and measured by Ostwald ; they were in the case of the sodium acetate as follows : For

$$\begin{array}{lll} (1) & n = 0.01321 & b = 0.00028 \quad c = 0.001737 \\ (2) & n = 0.02641 & b = 0.00138 \quad c = 0.00448 \\ (3) & n = 0.05282 & b = 0.00508 \quad c = 0.001142 \end{array}$$

and in the case of the sodium formate, for

$$\begin{array}{lll} (4) & n = 0.01414 & b = 0.00081 \quad c = 0.00133 \\ (5) & n = 0.02828 & b = 0.00278 \quad c = 0.00309 \\ (6) & n = 0.05657 & b = 0.00886 \quad c = 0.00714 \end{array}$$

By substituting these values and the values of the constants just preceding in the algebraic equation given above, the following six numerical equations were obtained :

$$\begin{array}{ll} (1) & x^3 + 0.08547 \ x^2 - 0.001303 \ x + 0.01859 = 0 \\ (2) & x^3 + 0.0800 \ x^2 - 0.002606 \ x + 0.0985 = 0 \\ (3) & x^3 + 0.0661 \ x^2 - 0.005134 \ x + 0.04835 = 0 \\ (4) & x^3 + 0.004830 \ x^2 - 0.0001095 \ x + 0.01224 = 0 \\ (5) & x^3 + 0.001296 \ x^2 - 0.0002059 \ x + 0.05787 = 0 \\ (6) & x^3 - 0.006802 \ x^2 - 0.0003625 \ x + 0.02549 = 0 \end{array}$$

Estimated values of  $x$  were substituted in these equations till the roots were found ; and from the latter the solubility was calculated by the equation :  $m = x + m_0(1 - a_0)$ . The solubility values so calculated are placed in the following table by the side of the mean values experimentally determined. In the last column the percentage differences between the two series of values are given.

#### SOLUBILITY OF BENZOIC ACID IN SODIUM ACETATE SOLUTION.

Number.	Concentration of the salt.	Calculated solubility.	Found solubility.	Percentage difference.
1.....	0.00000	0.02793	0.02793	.....
2.....	0.01321	0.03846	0.03878	+0.82
3.....	0.02641	0.04783	0.04840	+1.19
4.....	0.05282	0.06380	0.06480	+1.52

#### SOLUBILITY OF BENZOIC ACID IN SODIUM FORMATE SOLUTION.

Number.	Concentration of the salt.	Calculated solubility.	Found solubility.	Percentage difference.
1.....	0.00000	0.02793	0.02793	.....
2.....	0.01444	0.03423	0.03456	+0.96
3.....	0.02828	0.03858	0.03888	+0.77
4.....	0.05657	0.04553	0.04530	-0.50

The tables show that the agreement between the found and the calculated solubility is satisfactory. The correctness of the principles of solubility-effect and of the laws of dissociation involved in the equation used for the calculation is therefore demonstrated.

As the equation given above is quite complicated, and as the determination of the values of  $b$  and  $c$  involved is a laborious operation, it is important to show that approximately accurate results can be obtained when these quantities are neglected. In this case equation (1) becomes simplified to the following equation :

$$x^3 + rx^2 - (rn + k_a)x - k_ar = 0. \quad (2)$$

The values of the solubilities calculated by the equation are given in the following table, together with those calculated by equation (1), and with the percentage differences between the two values. The first three columns of figures show the solubility in the three sodium acetate solutions, the last three that in the sodium formate solutions.

#### CALCULATED SOLUBILITIES.

By equation (1).....	0.03846	0.04783	0.06380	0.03423	0.03858	0.04553
By equation (2).....	0.03844	0.04798	0.06392	0.03384	0.03801	0.04391
Percentage difference	0.05	0.30	0.20	1.14	1.48	3.60

It will be seen that in the case of the sodium acetate solutions the solubility values calculated by the simpler formula are almost identical with those obtained by means of the exact formula. In the case of the formate the differences are greater, but only for the greatest concentration is it at all considerable (three and six-tenths per cent.). Therefore for acids not more soluble than benzoic acid, when dissolved in salt solutions of corresponding concentrations, the simpler equation would be sufficiently exact for most purposes.

## THE COLOR OF SULPHUR VAPOR.<sup>1</sup>

BY JAS. LEWIS HOWE AND S. G. HAMNER.

Received August 29, 1898.

OUR attention was some time since called to a curious difference of opinion on the part of chemical authorities as to the color of sulphur vapor. In twenty-nine standard text-books and reference books examined which mention the color of the vapor, thirteen different colors are given, as follows:

	Authorities.
Deep yellow .....	4
Orange .....	5
Orange to dark yellow .....	1
Orange-yellow .....	2
Brownish yellow.....	6
Yellowish brown.....	1
Amber.....	2
Yellowish red.....	1
Red.....	1
Deep red.....	2
Deep red to brown .....	1
Brownish red.....	2
Reddish brown.....	1

In no work was any mention found of a change in the color of the vapor with changing temperature.

In order to examine the true color of the vapor a number of experiments were carried out, which, while not complete or entirely satisfactory, nevertheless throw some light upon the discrepancies cited. The first apparatus used consisted merely of a small test-tube of hard glass, within a larger tube, also of hard glass, the smaller tube being held free from contact with the larger by means of a wire frame. The ends of both tubes were stopped with asbestos wads to prevent free circulation of the air. A piece of roll sulphur was placed in the inner tube and heated by Bunsen burners. The pure sulphur vapor could be seen in the inner tube, the hot air in the outer tube preventing the condensation of the vapor on the sides. This simple apparatus gives a good view of sulphur vapor up to the softening point of the glass. The second form of apparatus used was

<sup>1</sup> Read at the Boston meeting of the American Chemical Society, August, 1898.

a porcelain tube two cm. in diameter and sixteen cm. long, with the ends covered by thin sheets of mica, and the whole tightly packed in a larger iron tube by clay. The inner tube was thus not sealed perfectly, but permitted the escape of the excess of sulphur vapor on heating, though under some considerable pressure. The apparatus was heated in a muffle whose rear end was replaced by a sheet of mica. It was thus possible to have a clear view through the tube while it was heating. The temperature was gauged approximately by tubes of silver chloride (melting-point  $457^{\circ}$ ), lead chloride (melting-point  $498^{\circ}$ ), and potassium iodide (melting-point  $634^{\circ}$ ).

In every case the sulphur, when just beginning to boil, gave a vapor which would perhaps be denominated orange-yellow. This color is almost exactly matched by a normal solution of potassium bichromate. As the temperature increases the color very rapidly deepens and loses every vestige of the yellowish tint. This corresponds to a temperature not much above  $457^{\circ}$ . On raising further the temperature, the color deepens further. The deepest color was found by several experiments to be at the temperature of about  $500^{\circ}$  (lead chloride just fused). The paler red color is matched by a solution consisting of

	Parts.
Ferric chloride (normal solution).....	1
Potassium thiocyanate (normal solution).. <td>2</td>	2
Water .....	312

The deepest red is matched by a solution :

	Parts.
Ferric chloride (normal solution).....	1
Potassium thiocyanate (normal solution).. <td>2</td>	2
Water.....	250

This is as far as the changes can be observed in the test-tubes. Heated in the muffle, immediately above  $500^{\circ}$ , the vapor begins to grow perceptibly lighter, at  $634^{\circ}$  being almost straw-color. Up to this temperature the escaping jet of sulphur vapor indicated that the tube must be filled with sulphur vapor. When this jet ceased the results became too doubtful to record. That the rapidly decreasing intensity of color was not due merely to decreasing pressure is evidenced by the fact that the color of the vapor at its darkest point was almost exactly the same in the



porcelain tube and in the test-tube, in the latter case the vapor being practically at atmospheric pressure.

The cause of the different colors applied to sulphur vapor is doubtless due to three causes :

1. The general difficulty of describing the colors of vapors, the relative intensity of which is so much less than that of our ordinary standards.

2. The fact that the color of sulphur vapor varies with the temperature.

3. Sulphur vapor condenses so readily that when boiled in a test-tube the sides of the tube are covered with a layer of the brownish red liquid, which has doubtless sometimes been mistaken for the vapor. Similarly, when sulphur fumes escape from a hot covered crucible into which sulphur has been thrown, it is the condensing sulphur mist, very deep red in color, which one sees, and not the true vapor of sulphur.

The conclusions of this paper are that the color of sulphur vapor varies with the temperature, being of an orange tint just above its boiling-point, deepening to a red which is strongest at 500°, and then becoming rapidly lighter with increasing temperature. The color at the boiling-point is that of a normal solution of potassium bichromate; that of the deepest red is that of a rather dilute solution of ferric thiocyanate.

It is hoped it may be possible to carry these experiments further, but no reservations are made of the subject if others are interested.

WASHINGTON AND LEE UNIV.,  
July 1, 1898.

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## THE FORMATION OF ALUMS BY ELECTROLYSIS.<sup>1</sup>

BY JAS. LEWIS HOWE AND E. A. O'NEAL.

Received August 20, 1898.

THE work herein described had for its special end the formation of alums of manganese, and while, in this particular, success was not attained, it is felt that it is well to place the work on record, especially as phases of it are capable of further development, from which interesting results may be hoped.

Manganese salts in which the metal is trivalent, are not very satisfactorily known. Potassium and ammonium manganic

<sup>1</sup> Read at the Boston meeting of the American Chemical Society, August, 1898.

alums have been described by Mitscherlich, but to manganic sulphate,  $\text{Mn}_2(\text{SO}_4)_3$ , Franke, who has most thoroughly studied

it, gives the formula  $\text{Mn}^{\text{II}} \left\langle \begin{array}{c} \text{SO}_4 \\ \text{SO}_4 \end{array} \right\rangle \text{Mn}^{\text{IV}} \text{SO}_4$ .<sup>1</sup> A salt of this consti-

tution could hardly give an alum, and the literature of the manganese alums is very unsatisfactory. It was hoped by using the oxidizing action of the electric current on a solution of manganous sulphate in the presence of an alkaline sulphate, manganic alum might crystallize out, and the reaction was studied with other metals for the sake of familiarity with the method and for comparison. Incidentally several alums were obtained and analyzed which have not been previously described.

*a. Iron Alums.*—Apparatus: Positive electrode, a platinum dish of about 250 cc. capacity resting on a coil of heavy copper wire; negative electrode, a coil of heavy platinum wire; diaphragm, the lower portion of the porous cup of a Bunsen cell. In different experiments different batteries were used, but Bunsen or crowfoot cells were generally used.

The following is a specimen experiment: Inner solution, ferrous sulphate strongly acidified with sulphuric acid; outer solution, saturated with ferrous sulphate and ammonium sulphate, and also strongly acidified with sulphuric acid; six crowfoot cells; current, 0.04 ampère. In forty-eight hours a large crop of beautiful iron-ammonium alum crystals, of perfect octahedral form, were produced. In one experiment with solutions as above and apparatus also, except that Bunsen cells were used, with current 0.02 ampères, forty-one grams of iron ammonium alum were obtained in twenty-four hours. This method is probably applicable to the formation of this alum on a commercial scale, having as its advantages the ease with which it is conducted and the fine quality of the product. Owing to the lesser solubility of potassium sulphate, the method, while successful, does not give such good results in the formation of iron potassium alum.

The formation of iron sodium alum was tried, using solutions as above, with sodium sulphate substituted for ammonium sulphate. Current, four Bunsen cells. After twelve hours the

<sup>1</sup> *J. prakt. Chem.* [2], 36, 451.

outer solution (+) was pink and in twenty-four hours had become dark purple, resembling almost a solution of potassium permanganate, while oxygen bubbles were given off at the positive pole. A little ferrous sulphate solution was added, at which the color at once disappeared, but after several hours with the current, it again became dark purple. The color disappeared at once with reducing agents. The color was that of ferrates, but the presence of ferric acid is hardly probable, and the solution being strongly acid, ferrates could not be present. It seems more probable that the compound was one of persulphuric acid. No crystals could be obtained even by using a freezing mixture. Some of the solution set aside for several weeks left, on evaporation, a hard, dirty, violet crystalline mass, containing crystals somewhat triangular in form, which were very insoluble in both water and hydrochloric acid. This substance was not pure and was not further investigated.

*Iron Rubidium Alum and Iron Cesium Alum*,  $\text{RbFe}(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$  and  $\text{CsFe}(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$ .—As no description of these alums was found in chemical literature, they were both formed and analyzed. In working with rubidium and cesium salts, a smaller form of apparatus was used, the positive pole being a platinum crucible of eleven cc. capacity, the negative pole a coil of heavy platinum wire, and the diaphragm an unglazed porcelain annealing cup. The cup was filled as above with a solution of ferrous sulphate and the platinum crucible, which rested in a ring of heavy copper wire, with a solution of ferrous sulphate and rubidium sulphate or cesium sulphate. Both solutions were strongly acid with sulphuric acid. Very considerable crops of both the rubidium and cesium alums were obtained in the form of small octahedra. They are of a delicate violet color, turning slightly greenish on exposure to the air. They resemble potassium alum in every respect except that the rubidium alum is very slightly soluble and the cesium alum almost insoluble in water.

Analysis :

	Calculated for $\text{RbFe}(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$	Found.	
		I.	II.
$\text{H}_2\text{O}$ .....	39.3	39.1	38.9
$\text{SO}_4$ .....	34.9	35.2	...
Fe .....	10.2	11.0	..

	Calculated for $\text{CsFe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ .	Found.	
		I.	II.
$\text{H}_2\text{O}$ .....	36.2	36.1	36.3
$\text{SO}_4$ .....	32.2	33.3	...
Fe .....	9.4	10.4	...

*b. Cobalt Alums.*—The cobalt, potassium, and ammonium alums were discovered by Marshall, whose work was the incentive to that described in this paper. The rubidium and cesium alums were made by us and have not been hitherto described. The apparatus used was the smaller form, as for the iron rubidium alum, and the experiments conducted similarly. The outer (positive) solution was kept quite strongly acid with concentrated sulphuric acid. Four Bunsen cells were used; current 0.16 to 0.19 ampère. At first it was found that in some experiments beautiful crystals were obtained in considerable quantity, in others no crystals at all. This was soon found to be due to the temperature. On nights when the laboratory was cool the crystals formed readily. By keeping the crucible with its support immersed in a beaker of water, ill effects from heating by the current were avoided and the alums readily obtained.

It is thus seen that the rubidium and cesium alums are much more readily formed than the potassium and ammonium, as would be expected. These alums are minute, deep blue octahedra, stable in dry air, but gradually decomposing in moist air with formation of cobalt sulphate; the cesium alum showed occasional cube faces. In water the alums are quickly decomposed with evolution of oxygen and reduction to cobalt sulphate. In dilute hydrochloric acid and in dilute sulphuric acid the crystals dissolve to a blue solution. In concentrated hydrochloric acid and concentrated sulphuric acid they are decomposed, giving in the latter case a brown solution.

Several methods of analysis were tried. On heating to  $200^\circ$  the salt becomes whitish pink, and apparently contains free sulphuric acid from its decomposition into cobalt sulphate, more or less water being thus retained. The best method of analysis was found to be the following: The salt is mixed with anhydrous sodium carbonate in a platinum boat, and heated in a combustion tube in an oxygen stream. The water is absorbed in a calcium chloride tube. The residue is treated with hot

<sup>1</sup> *Proc. Roy. Soc., Edin.*, 14, 203; *J. Chem. Soc.*, 59, 760.

water. The filtrate contains the Cs (or Rb) and the  $\text{SO}_4$ , which are estimated as cesium chloroplatinate and barium sulphate. The insoluble residue, cobalt oxide, is heated in a hydrogen stream and weighed as metallic cobalt.

	Calculated for $\text{RbCo}(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$ .	Found.	
		I.	II.
Rb .....	15.5	15.9	...
Co .....	10.7	11.9 <sup>1</sup>	...
$\text{SO}_4$ .....	34.8	35.4	...
$\text{H}_2\text{O}$ .....	39.1	37.9	38.22
	Calculated for $\text{CsCo}(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$ .	Found. <sup>2</sup>	
Cs .....	22.1		22.5
Co .....	9.8		10.2
$\text{SO}_4$ .....	32.0		32.2
$\text{H}_2\text{O}$ .....	36.0		36.7

*c. Chromium Alums.*—An experiment was tried using a solution of potassium chromate strongly acidified with sulphuric acid as electrolyte for the negative pole, and dilute sulphuric acid for the positive. After thirty-six hours no chrome alum was obtained, but considerable potassium sulphate was deposited, strongly colored green by the chromic solution present. On substituting ammonium chromate for the potassium chromate a considerable crop of chromium ammonium alum crystals was obtained at the negative pole. These crystals were very small. Four Bunsen cells were used in these experiments. This method of electrical reduction has been used by Piccini for the formation of vanadium<sup>4</sup> and titanium<sup>5</sup> alums.

*d. Experiments with Manganese.*—These experiments were carried out in both the large and small apparatus; with manganese sulphate and ammonium, rubidium, and cesium sulphates; with varying quantities of free sulphuric acid in the electrolytes; with different strengths of current; and at various temperatures. The solution at the positive pole in every case became deep wine color, and the higher oxide of manganese was deposited. In one case only were a few minute octahedral crystals found in a rubidium manganese solution. These were deep wine color and qualitatively contained manganese. It is not, however,

<sup>1</sup> As  $\text{CoSO}_4$  after removal of Rb as  $\text{Rb}_2\text{PtCl}_6$ .

<sup>2</sup> By loss at  $200^\circ$ .

<sup>3</sup> By method described above.

<sup>4</sup> *Gazz. chim. ital.* 25, [2], 451.

<sup>5</sup> *Ibid.*, 25, [2], 542.

improbable that these were crystals of common alum colored by manganese. In an experiment with ruthenium such crystals were obtained, the aluminum being probably derived from the porcelain diaphragm. In a number of cases the black precipitate at the positive pole, supposed to be manganese dioxide, when allowed to stand with concentrated sulphuric acid, showed itself under the microscope to be made up of flat, transparent, pale, wine-colored crystals, resembling elongated hexagonal plates. These are not readily soluble in water or acids. They were not further investigated.

The electrolytical method does not seem to be applicable to the formation of manganese alums from manganous salts.<sup>1</sup> It is hoped later to try the electrolytic reduction of manganates and permanganates.

*e. Experiments with Ruthenium.*—No crystallized oxy-salts of ruthenium are known. As the double salts of the trichloride crystallize well, an effort was made to obtain an alum by the electrolytic reduction of the nitrosochloride. The small apparatus was used. The solution at the negative pole was a solution of cesium ruthenium nitrosochloride,  $\text{Cs}_2\text{RuCl}_4\text{NO}$ ,<sup>IV</sup> which had been boiled some time with sulphuric acid, and which might be supposed to contain the nitrososulphate. It was hoped to reduce the nitroso group and split it off as ammonia, leaving trivalent ruthenium in the presence of sulphuric acid and cesium sulphate, the most favorable condition for alum formation. No sign of alum was found, nor did the electrolyzed solution show reaction for trivalent ruthenium. A considerable quantity of ruthenium tetroxide,  $\text{RuO}_4$ , was given off. This was probably owing to oxidation at the positive pole, some of the ruthenium solution having penetrated the diaphragm into the sulphuric acid which surrounded the positive pole. The formation of ruthenium tetroxide by electrolytic oxidation has not been pre-

<sup>1</sup> Since the above was in type, a further article by Piccini has appeared in the *Zeitschrift für anorganische Chemie*, 17, 361, describing the formation of the cesium manganese alum by electrolytic oxidation, in a method apparently like that described in this paper. No particulars regarding current, etc., are given. This would seemingly settle the question of the trivalence of manganese in manganic salts. Attention is called, as in our paper, to the advantage in using rubidium and cesium compounds where it is desired to obtain difficultly crystallizable compounds. Piccini's result renders it probable that the few octahedra obtained in our rubidium manganese experiment were really rubidium manganese alum; he also found his alum contaminated by aluminium from the diaphragm.

viously noticed. Further experiments with other ruthenium compounds are being carried on.

WASHINGTON AND LEE UNIV.,  
July 1, 1898.

## ON THE DETERMINATION OF UNDIGESTED FAT AND CASEIN IN INFANT FECES.<sup>1</sup>

BY HERMAN POOLE.

Received August 29, 1898.

LAST summer I had the honor of presenting to the Society a paper on "Methods of Determining Fat and Casein in Feces."<sup>2</sup> In that paper I mentioned the method I had adopted in the investigation I was then engaged in, and stated why the methods previously used did not give me satisfactory results. This paper may be considered as a sequel to that one, or perhaps more correctly, a résumé of the work I have done on the subject to this time. The methods given in the paper cited were used substantially as there given throughout all the cases, no better one having been suggested; in fact, my requests for other methods met with no response at all, showing that but little work had been done directly on this line.

The methods of analysis used may be briefly stated as follows: The feces were carefully removed from the containers as well as possible and thoroughly mixed, if practicable. A portion of this was then weighed out and dried in an air-bath at 90° C. for one hour, and afterwards at 105° to 110° C. for two or three hours or until of constant weight. A portion of this dried residue was then treated with ether in a Soxhlet extraction apparatus to extract the fat and other substances soluble in ether. The extract so obtained was evaporated at 100° till dry and usually weighed. This weighing was not done in every case as it had no important bearing on the aim of the investigation, which concerned the undigested fat and casein only. After drying, the extract was saponified with alcoholic potash, a small portion generally remaining undissolved. Water was then added and the whole boiled till the alcohol had been expelled. Practically this was carried on until the mass was nearly dry, water having

<sup>1</sup> Read at the Boston Meeting of the American Chemical Society, August, 1898.

<sup>2</sup> This Journal, 19, 877.

been added during the boiling. The solution was then diluted with water and filtered.

The cholesterol being soluble in ether was then taken up by agitation in a separatory globe with that solvent. On allowing the mixture to rest the two liquids separated readily, especially after a reagitation. The treatment with ether was generally repeated once, occasionally twice. The second repetition was hardly necessary, as only traces were taken up.

The solution thus freed from cholesterol was evaporated nearly dry, dissolved with water, and the fat acid determined as usual by precipitation with mineral acid, collecting, and weighing. The solution was usually clear enough without filtration.

In many cases the cholesterol solution in ether was evaporated and that body determined. As this was only of minor interest and not germane to the investigation, it was done only when it did not interfere with other work. No regular ratio of the fat and cholesterol could be established.

The solid residue from the ether extraction was treated successively with water and alcohol and then dried at 100° C. This dried residue was afterwards digested in a mixture of equal parts of water and hydrochloric acid for some ten or twelve hours at a temperature of about 60° C. This dissolved the casein and at the same time decomposed the earthy fat acid compounds, and, on cooling, a collection of fat acid was always found. No attention was paid to this fat acid as, being in combination with bases, it was considered to have been digested or changed in the system, and only undigested fat was sought. This fat acid was quite hard and usually, though not always, nearly white in color.

After cooling the solution of casein and filtering, it was evaporated to dryness and the nitrogen determined by the Kjeldahl method. The casein was estimated as being  $\frac{1.00}{1.8}$  of the nitrogen so determined.

The results obtained are shown in the accompanying table, which contains the results from most of the cases examined :



## CASE I.

	Reaction.	Quantity.	Water.	Fat. <sup>1</sup>	Cholesterol. <sup>1</sup>	Casein. <sup>1</sup>
		Grams.	Per cent.	Per cent.	Per cent.	Per cent.
1	Acid.....	28.0	67.7	17.52	11.25	3.28
2	Acid.....	23.0	75.0	18.88	8.40	4.24
3	Acid.....	26.0	73.3	14.23	5.11	4.35
4	Acid.....	30.0	76.1	9.86	6.50	5.02
5	Faint acid .....	29.0	68.8	7.11	3.68	3.67
6	Nearly neutral..	10.8	69.9	12.65	5.92	3.52
7	Neutral .....	35.7	65.0	9.26	6.24	...
8	Neutral .....	38.6	65.0	8.54	7.61	3.11
9	Faint acid.....	62.5	55.0	5.53	5.01	2.87
10	Faint acid.....	42.6	71.5	8.63	5.17	...
11	Faint acid.....	15.8	63.2	8.55	4.99	3.81
12	Very faint acid .	51.8	51.2	...	2.57	3.16
13	Neutral .....	33.0	61.2	6.44	3.21	4.77
14	Acid.....	21.0	75.0	11.68	7.50	6.00
15	Neutral .....	18.4	70.6	13.57	4.43	6.00
16	Very faint acid .	29.0	69.3	11.06	5.81	7.97
17	Very faint acid .	23.4	63.0	9.86	8.91	5.19
Average .....		27.96	67.2	10.90	6.39	5.03

## CASE II.

1	Acid.....	9.8	77.95	24.14	22.76	8.24
2	Faint acid.....	5.2	60.00	12.98	7.69	7.65
3	Faint acid.....	7.7	72.83	14.76	15.31	7.54
4	Faint acid.....	33.44	65.14	8.84	8.11	5.81
5	Faint acid.....	19.36	70.20	10.57	6.63	3.68
6	Neutral .	6.6	65.66	8.74	10.11	4.48
7	Acid.....	12.6	69.18	10.67	9.14	6.04
8	Faint acid.....	8.76	74.86	11.27	20.11	4.97
9	Acid.....	10.56	75.18	13.09	20.85	7.21
10	Faint acid.....	9.32	76.14	14.44	....	8.95
11	Faint acid.....	3.12	79.69	22.11	....	...
12	Faint acid.....	17.13	71.84	12.18	15.10	8.59
Average .....		11.92	71.57	14.47	13.58	6.65

## VARIOUS SAMPLES.

1	Faint acid.....	{ about five grams	78.40	9.17	12.80	16.39
2	Faint acid.....		75.45	19.81	10.91	12.22
3	Acid.....		53.25	8.98	16.15	5.68
4	Faint acid.....		46.55	9.57	4.85	6.31
5	Faint acid.....		20.0	73.00	8.25	13.15

<sup>1</sup> These are calculated on the dry material.

The reaction with litmus was almost uniformly acid, although seldom strong enough to admit of determination. In a few cases no action was noticed and in a very few a slightly alkaline reaction was observed. It is possible that these alkaline cases may have been due to decomposed urine, all the samples being old (*i. e.*, more than one day).

The quantity excreted varied considerably, but the quantity as given in the table does not show the actual quantity voided. It simply shows the amount available for analysis, and in many instances this was only a small percentage of the entire amount, but from physical reasons it was impossible to obtain any more in a clean condition, free from extraneous substances. The quantity column of Case I fairly represents the actual amounts per day.

The amount of moisture varied considerably and its determination was generally of no use except as a means of reducing the subsequent results to a dry basis. Many of the samples were fairly fresh and in such cases a percentage of about seventy was attained. Departures far from this amount occurred only in old and partially dried samples.

The quantity of fat, casein, and cholesterol varied considerably. Not only is a large variation noticeable between the different individuals but also in the same case from day to day. There seems to be no relation existing between the proportions of these three, except that generally a large amount of fat is accompanied by a correspondingly large amount of casein. This could be expected, as the presence of an increase in one would be caused by a derangement of the intestinal canal and should have an effect on the other also. This is quite evident in the latter part of the data from Case I. In this instance the removal of the child to the country had a marked and unmistakable effect on the feces; still, the child was reported in good health.

Incidentally, it may be mentioned that the characteristic odor of adult feces was entirely wanting. It showed itself in one instance only, and this case was dismissed for that reason. Subsequent investigation showed that the child had been fed on a mixed diet. Indol and skatol were looked for but not formed except in the case just mentioned.

All the children were fed on the same kind of milk, and given approximately the same quantities per day. This milk was not a single cow's milk but a milk prepared by the "Gaertner Mother Milk" method from the average milk of a large number of cows, and care was taken to have the milk as near as possible of the same composition. The analysis of the milk was approximately

	Per cent.
Fat .....	3.05
Casein.....	2.09
Lactose .....	6.00
Specific gravity,	1.0275.
Reaction,	faintly alkaline.

The milk was sterilized perfectly and did not become sour after standing exposed for three days.

Each child consumed from one to one and one-third liters daily and hence ingested

	Grams.
Fat .....	30.5 to 40.67
Casein .....	20.9 to 27.87
Lactose .....	60.0 to 80.0

Cases I and II were well cared for throughout the investigation and the results obtained may be considered as reliable as possible from such cases. The others are given to show the range of results obtained, but from reasons beyond the control of the investigation, modifying influences were present; and, while the analytical results are individually correct, the connection between the food ingested and the excreta cannot be traced.

## ELECTRIC FURNACES FOR THE 110-VOLT CIRCUIT.<sup>1</sup>

BY NEVIL MONROE HOPKINS.

Received August 29, 1898.

IT occurred to the writer in wiring a couple of experimental arc lamps across the feeders of an incandescent lighting system, that a laboratory electric furnace could be operated on a series carbon plan, without disturbing the protecting fuses of the circuit. The idea of focusing a pair of arcs within a small crucible, or furnace, using only the amount of resistance located in the tops of typical series lamps, proved, however, to be unsatis-

<sup>1</sup> Read at the Boston meeting of the American Chemical Society, August, 1898.

factory, the current absorbed becoming abnormal, upon introducing a charge for fusion, when its character embodied fair electrical conductivity. To obviate this difficulty, as well as to compensate for the lowering of resistance due to eddy currents between the poles when run in combination with a charge rich in carbon, or graphite, as in the making of calcium carbide, a third pair of electrodes was placed in series, together with a variable rheostat in place of the resistance wire of the lamps. With this arrangement, calcium carbide was readily prepared on a laboratory scale, using only a twelve ampère fuse wire in each leg of the feeding conductors, and allowing the separation of the electrodes through a distance of three and one-half inches. The charge of lime and coke was finely ground together in an iron mill before feeding into the furnace, insuring a homogeneous body. It may be of interest to state in connection with this work that lime and charcoal are poorly adapted for the purpose, the charcoal, because of its floury nature, oxidizing rapidly away from the lime without combining with it. Fig. 1 illus-

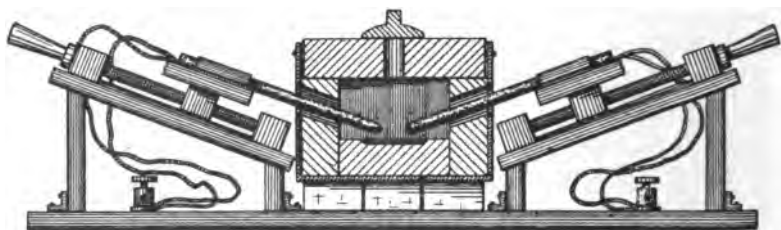


FIG. 1.—Elevation of "Series Carbon" Laboratory Electric Furnace.

trates the "series carbon" furnace in elevation and partial section, showing a simple construction. Fig. 2 gives a plan view

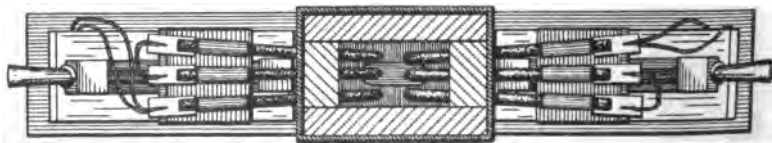


FIG. 2.—Plan View of Furnace with Cover Removed.

of the apparatus with the cover of the furnace proper removed. This furnace, which consists of an iron shell, lined with fire-clay, should not be over twelve inches long if intended

for use with ordinary electric light carbons, because of their limited reach. The screw mechanism of this "plant" is readily put together by cutting into sections a large furniture-maker's clamp, using the unthreaded portions for the end bearings, and the two threaded sections for the center pieces, which travel back and forth. The carbon electrodes are conveniently mounted on a block by means of tightly-fitting brass tubes, attached in turn with staples or "straps" and screws. Contact is made with the ends of the carbons by pushing brass spring jacks under their ends, to which the connections are soldered. These pieces of spring brass allow of the rapid adjustment of the carbon pencils, or their removal when too short for further use. To start the furnace, when properly connected, it is necessary to feed the electrodes into the furnace until they are all in good contact, and strike the wooden incline planes with a mallet, which causes the ends of the carbons to vibrate or rub together, and make good contact. When the arc has once formed the furnace may be handled like an ordinary single carbon equipment. The method of wiring is given in Fig. 3, where M represents the

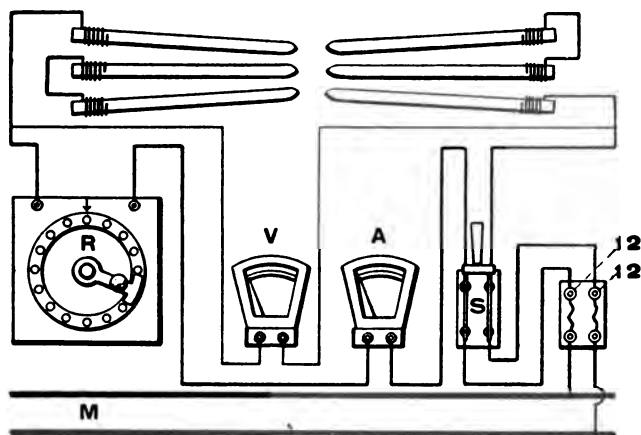


FIG. 3.—Diagram of Connections with 55- or 110-Volt Lighting Circuit, with Ammeter and Voltmeter Arranged for Studying the Behavior of Bodies within the Arc.

main feeders, with a fuse block connected at the right, carrying a pair of twelve ampère fuses. The knife switch S is an important feature, and should be within easy reach of the furnace. The ammeter A and the voltmeter V are included as a matter of

interest, and afford a ready means of watching the behavior of different bodies with the arcs. The variable rheostat, R, completes the equipment, which must also be in easy reach of the furnace. In order to avoid annoyance from intermediate fuses, the apparatus should be connected, as near the meter as possible, if the current is sold on this plan. Should one of the twelve ampère fuses melt out, it should be replaced by another of the same capacity, and a little more resistance put in by means of the variable rheostat. Of course, fifteen and twenty ampère fuses may be used if desired, the twelve ampère size being about the smallest for the fusion of compounds possessing carbon as one of the ingredients. Should the variable rheostat at hand prove of too low a resistance for the preservation of the twelve ampère fuses, a second rheostat may be placed in series with it, although with the triple arc arrangement this will seldom be necessary. Fig. 4 illustrates a method for using a sin-

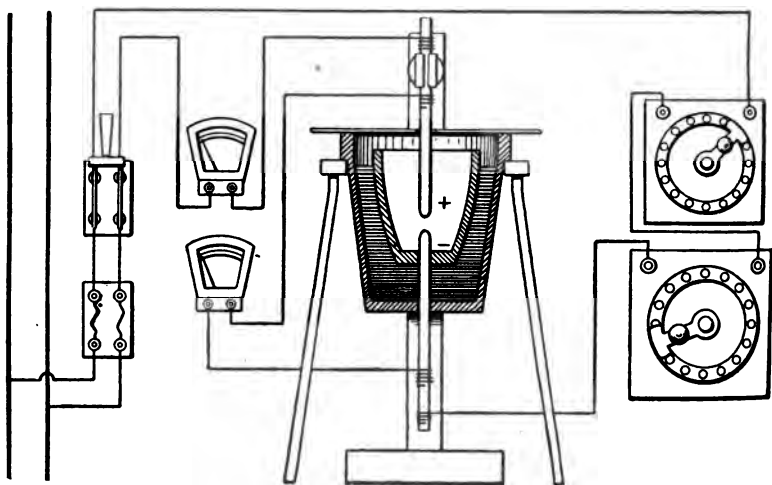


FIG. 4.—Method of Using Single Carbons for making Alloys and Small Fusions. 55- or 110-Volt Circuits.

gle pair of carbons for making alloys and other small fusions. Here, at least, two large rheostats will be necessary, and fuses of larger capacity must be employed. The small crucible is drilled through the bottom, receiving the lower electrode with a tight fit. The outer casing of the furnace in this instance consists simply of a large flower-pot filled in with some poor conductor of

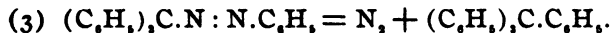
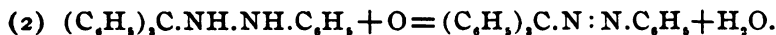
heat. The ammeter gives the total current absorbed, and the voltmeter the electromotive force at the arc. With this simple arrangement, copper and brass are easily melted, as well as iron and steel. As to the adjustment of the carbons, it is only necessary to feed the upper one down a fraction of an inch every two or three minutes. Should rheostats not be at hand, a bank of thirty-two C. P. lamps arranged in multiple and joined in with the furnace, answer the purpose for smaller fusions, and for metals possessing lower melting-points. By using ten 32 C. P. lamps in parallel, a good arc may be maintained, sufficient for small reductions, etc. Should three of these "flower-pot" furnaces be placed in series, the principle of the large furnace will obviously be brought into play, if some means is devised for controlling the upper carbons simultaneously.

### ON TETRAPHENYLMETHANE.<sup>1</sup>

BY M. GOMBERG.

Received August 29, 1898.

ABOUT a year ago<sup>2</sup> I reported a method by which small quantities of tetraphenylmethane were obtained, a substance which it had been proved impossible to prepare by the usual reactions.<sup>3</sup> The method consisted in oxidizing triphenylmethanehydrazobenzene to the corresponding azo-compound, and heating the latter to 110°–120° C. The reactions can be summarized by the following equations:



Unfortunately, the yield was very small, and even then the substance could be obtained only with difficulty.

The work has since been subjected to a revision, but with no better results in so far as the yield of tetraphenylmethane is concerned.

<sup>1</sup> Read at the Boston meeting of the American Chemical Society, August, 1898.

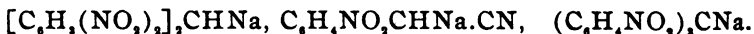
<sup>2</sup> *Ber. d. chem. Ges.*, 30, 2043, 1897.

<sup>3</sup> Haemilian, 1874: *Ber. d. chem. Ges.*, 7, 1209; Friedel and Crafts: *Compt. rend.*, 1877, 153; *Ann. chim. phys.*, 1884, 1, 497; E. and O. Fischer, 1878: *Ann. Chem. (Liebig)*, 194, 254; Magati, 1879: *Ber. d. chem. Ges.*, 12, 1468; Schwartz, 1881: *Ber. d. chem. Ges.*, 14, 1523; Waga, 1894: *Ann. Chem. (Liebig)*, 282, 330; Weisse, 1895: *Ber. d. chem. Ges.*, 28, 1537.

The method of oxidizing the hydrazo- to the azo-body has been greatly improved, and was found to be of general application for the preparation of azo-derivatives of this class.<sup>1</sup>

A mere elementary analysis is not sufficient to establish the composition of tetraphenylmethane, as the percentage of carbon and hydrogen is almost the same as that in triphenylmethane, and in other phenylated methane and ethane derivatives. A redetermination of the *molecular weight* seemed therefore very desirable, inasmuch as only about one-tenth gram of the substance was at my disposal for the first determination. The amount employed this time was again small, about 0.124 gram. It was nearly all recovered, and used for the preparation of a nitro-compound, furnishing, *quantitatively*, a tetranitro-derivative.

It has been shown by V. v. Richter<sup>2</sup> that the accumulation of nitro-groups in phenylmethanes imparts to these compounds sufficient negative character, so that they form salts with caustic potash, and especially with sodium ethylate. These salts are intensely colored, usually dark violet. They are formed by the replacement of sodium for the methane-hydrogen, giving, for example,



This reaction with triphenylmethane is exceedingly characteristic,—a fragment of a crystal of trinitrotriphenylmethane dissolves in sodium ethylate with a fine violet color.<sup>3</sup> The nitro-derivative, however, obtained from tetraphenylmethane, does not give any colored salts with caustic alkali or with sodium ethylate, even on heating. This is strong corroborative evidence of the constitution of tetraphenylmethane, showing that all the four hydrogen atoms in methane must have been replaced.

When the nitro-compound is treated with acetic acid and zinc dust, it shows the characteristic fuchsin reaction. Three to four milligrams suffice for this test. Lack of material prevented from fully identifying the dye as pararosanilin, since all this work, including the molecular weight determination, was performed on about two-tenths gram of tetraphenylmethane. An alcoholic

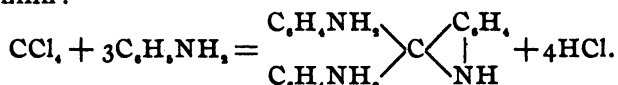
<sup>1</sup> See next paper : This Journal, 20, 780.

<sup>2</sup> *Ber. d. chem. Ges.*, 21, 2470, 2475, 1888.

<sup>3</sup> Trinitrotriphenylcarbiuol gives the same reaction on warming.



solution of the dye gave the same absorption spectrum as pararosanilin, prepared under exactly similar conditions directly from triphenylmethane. The formation of a rosanilin dye, involving, as it does, a splitting off of a *p*-amidophenyl group, is not so very surprising, when we consider the great tendency for the formation of such dyes under the most varied conditions. The historic reaction of Hofmann,<sup>1</sup> which led to the discovery of the rosanilin group, may be cited in this connection. By the action of anilin upon carbon tetrachloride, he obtained not the expected tetraamidotetraphenylmethane,  $(C_6H_4NH_2)_4C$ , but *p*-rosanilin:



The formation of the pararosanilin or a rosanilin-like dye, from the tetranitrotetraphenylmethane shows, that at least three nitrogen groups are in *para* position to the central carbon atom. And it is quite probable that the fourth nitro-group also occupies the *para* position.

#### EXPERIMENTAL PART.

*Triphenylmethaneazobenzene*,  $(C_6H_5)_3C.N:N.C_6H_5$ .—The hydrazo-derivative was obtained by the action of phenylhydrazine upon triphenylbrommethane, in an ethereal solution, with a yield of seventy to eighty per cent. of the theoretical quantity. It has been stated before,<sup>2</sup> that of all oxidizing agents tried, amyl nitrite gave the best results in oxidizing the hydrazo to the azo-body. But even with amyl nitrite the oxidation sometimes goes too far, especially if larger quantities are worked with at one time. In such cases a considerable amount is oxidized to triphenylcarbinol, and a portion is entirely decomposed. It was now found that the substitution of nitrous acid gas for amyl nitrite gives much better results. The hydrazo-compound is dissolved in ether, and nitrous acid gas is passed in, until the solution turns milky and shows signs of boiling. The solution is allowed to stand about half an hour. On concentrating, the azo-derivative separates in large, bright yellow crystals, melting at  $110^\circ$ – $112^\circ$  C. The yield is very satisfactory.

<sup>1</sup> *Compt. rend.*, 47, 492.

<sup>2</sup> *Ber. d. chem. Ges.*, 30, 2045, 1897.

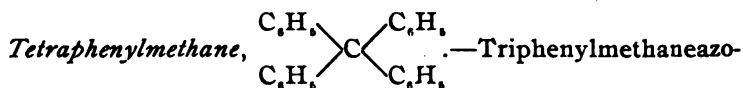
Seventeen grams of the hydrazo-body furnished by this method 14.5 grams of the azo-compound.

*Action of Bromine.*—When bromine is added to a solution of the azo-compound in chloroform, a heavy dark oil separates, which, after standing for some time, changes to a crystalline perbromide on stirring. The addition of a little petroleum ether hastens greatly the crystallization. The crystals obtained in this way were filtered, washed with a little chloroform and petroleum ether, and rapidly dried *in vacuo*. The inner portion, showing no decomposition by loss of bromine, was analyzed. The "perbromine" was estimated by suspending weighed samples of the perbromide in a solution of potassium iodide in water, and titrating the iodine with a standard solution of sodium thiosulphate.

	Calculated for (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> CB <sub>2</sub> Br <sub>2</sub>	Found.
Perbromine.....	55.33	54.85

When the perbromide is exposed to the air, it loses bromine, and leaves a white powder, which consists for the most part of triphenylbrommethane. On boiling the perbromide with alcohol, triphenylcarbinol was obtained (melting-point 158° C.)

The existence of such a perbromide is made quite probable by the existence of an analogous periodide.<sup>1</sup> Indeed, triphenylbrommethane itself, treated in a chloroform solution with bromine, gives also a crystalline perbromide, with similar properties and of the same composition as the perbromide described. This reaction is to be further studied.



benzene behaves in many respects like a true mixed fatty-aromatic azo-body. Thus, when heated to its melting-point, it decomposes with evolution of nitrogen, the amount of gas given off being quantitative.<sup>2</sup> The decomposition this time has been carried out as follows: About ten grams of pure clean sand, which had been thoroughly washed with benzene, was placed in a small flask and heated in an oil-bath to 110°–120° C. Fifteen grams of the finely powdered azo-compound was then gradually

<sup>1</sup> This Journal, 20, 790.

<sup>2</sup> *er. d. chem. Ges.*, 30, 2045, 1897.

added, a little at a time, with constant stirring. When no further evolution of gas could be noticed, the mass was extracted with hot benzene, filtered, and the solution concentrated on the water-bath. The residue consisted of a very thick, dark mass. This was divided into two portions. To one portion a very little benzene was added, and the sirupy mixture was allowed to stand until crystallization set in, in about four or five days. The small crop of crystals was separated from the mother-liquid by filtration on a pump and washed on a porous plate with a little petroleum ether. It was then recrystallized several times from small quantities of hot benzene, until absolutely white and of a constant melting-point. The yield of the pure substance was a little over two-tenths gram. The molecular weight determination was made with this material. The mother liquor, after several weeks' standing, furnished another crop of the tetraphenylmethane, which, when purified, will probably amount to about one-tenth gram.

The second portion of the original dark mass, as obtained from the decomposition of the azo-compound, was subjected to distillation *in vacuo*, at fifteen to eighteen mm. The temperature of the metal-bath was allowed to go up to 320° C. The distillate, which amounted to about one-half of the quantity taken, presented a dark-yellow viscous mass. On standing, a small quantity of triphenylmethane crystallized out. The rest, as well as the residue in the distilling flask, could not be brought to crystallization. No diphenyl or diphenylmethane could be detected.

*Molecular Weight.*—As naphthalene had given very good results in the first determination, the same solvent was chosen again for the cryoscopic method. It has the advantage when small quantities of the substance are at one's disposal, because of its high constant. Trials with triphenylmethane had shown that the naphthalene was pure, and that very good results could be obtained with this solvent.

Solvent : Benzene.

$$\text{Formula : } \frac{69 \times p}{d} = m.$$

$p$  = per cent. of substance in solvent.

$d$  = depression.

Tetraphenylmethane,  $m = 320$ .

Solvent. Gram.	Substance. Gram.	$\rho$ .	$d$ . °C.	$m$ .
9.427	0.1239	1.314	0.285	318

The tetraphenylmethane as now obtained has been found to agree in all properties with the substance previously reported. It is insoluble in ether, chloroform, petroleum ether, glacial acetic acid. Fairly soluble in hot benzene, but very little in the cold. It crystallizes from benzene in white, glistening needles. The melting-point, determined this time in a closed dish and with a normal thermometer, was found to be  $272^{\circ}$  C. instead of  $267.5^{\circ}$  C., as given before.

*Recovery of the Tetraphenylmethane.*—Nearly all the quantity employed in the determination of the molecular weight was recovered. The naphthalene was placed in a crystallizing dish and sublimed off at the lowest possible temperature. The residue was boiled out first with a little petroleum ether, and then thoroughly washed with ether. The white silky residue showed the correct melting-point of tetraphenylmethane, and amounted to 0.1075 gram.

TETRANITROTETRAPHENYLMETHANE,  $(C_6H_4NO_2)_4C$ .

The quantity of tetraphenylmethane recovered from naphthalene after the determination of the molecular weight, was nitrated. The nitration was done according to the method employed by E. and O. Fischer<sup>1</sup> for the preparation of *para*-trinitrotriphenylmethane. The hydrocarbon was added in small quantities to two cc. of nitric acid (sp. gr. 1.50), cooled in ice-water. The substance dissolved very readily. The bright yellow solution was allowed to stand about fifteen minutes. On the addition of water the nitro-compound separated in white minute crystals, without the slightest trace of any oily, sticky by-products, as is always the case when triphenylmethane is nitrated. The crystalline precipitate was separated by means of a pump, thoroughly washed with water, alcohol, and finally with a little ligroin, and dried *in vacuo* over sulphuric acid. The yield was 0.166 gram, while theoretically 0.107 gram of tetraphenylmethane should yield 0.1669 gram of the tetranitro-derivative.

The substance was analyzed with the following results :  
0.1417 gram gave 14.8 cc. nitrogen at  $24^{\circ}$  and 737 mm.

<sup>1</sup> *Ann. Chem.* (Liebig), 194, 254.

	Calculated for (C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> ) <sub>4</sub> C.	Found.
N .....	11.20	11.68

The nitro-derivative, as already mentioned, consisted of minute, white, needle-like crystals. It is insoluble in ether, petroleum ether, alcohol; insoluble in cold glacial acetic acid, and only slightly when heated. It is somewhat soluble in hot benzene and hot chloroform, from either of which solvents it can be obtained in a nice crystalline form. It begins to darken at about 268° C., and melts at 275° C.

Unlike the trinitrotriphenylmethane, or the trinitrotriphenylcarbinol, it does not dissolve in sodium ethylate, nor does it give any coloration with it even on heating. The non-formation of colored alkali salts, as well as the high melting-point, show the absence of any nitrotriphenylmethane.

The nitration of the hydrocarbon has been repeated several times on small quantities, five to ten milligrams, of the original tetraphenylmethane, which had not been employed for the determination of the molecular weight, but the results were in every respect identical with those described above.

*Reduction to a Rosanilin Dye.*—About five milligrams of the nitro-compound were dissolved in boiling glacial acetic acid, and zinc dust gradually added in small quantities. On the first addition of the zinc the solution turned a bright red, and the reduction to a colorless base required considerable zinc dust and boiling. The solution was diluted with water, filtered from the excess of zinc dust, treated with excess of ammonia, and the precipitated colorless leuco-base was filtered and washed. The base was then gently ignited with a few drops of concentrated hydrochloric acid on a platinum foil, according to the method of E. and O. Fischer<sup>1</sup> for triphenylmethane. The characteristic fuchsin color so developed could not be distinguished at any stage from that produced by the reduction-product of *p*-trinitrotriphenylmethane. The two were reduced in about the same quantities and under the same conditions. The two dyes were dissolved in about the same amount of alcohol, and when examined spectroscopically, gave about the same absorption bands.

Lack of material prevented me from establishing the identity of the dye.

<sup>1</sup> *Ann. Chem.* (Liebig), 194, 273.

The subject will be continued, and it is hoped that perhaps larger quantities of tetraphenylmethane will be obtained by the action of triphenyliodomethane upon mercury-diphenyl.

ANN ARBOR, MICHIGAN.

## HYDRAZO- AND AZO-DERIVATIVES OF TRIPHENYLMETHANE.<sup>1</sup>

BY M. GOMBERG AND A. CAMPBELL.

Received August 29, 1898.

ONE of us has recently<sup>2</sup> described a method by which small quantities of tetraphenylmethane were obtained. The method involved the synthesis of triphenylmethaneazobenzene, which was obtained by the oxidation of the corresponding hydrazo-derivative. The azo-body, on being heated to 110°-120° C., loses nitrogen, and furnishes, among other products, tetraphenylmethane.

The present work was undertaken with the hope of obtaining substitution derivatives of tetraphenylmethane, by subjecting substituted azo-compounds of triphenylmethane to the same treatment as the simple azo-compound itself. For the present, we shall only give a description of the hydrazo- and azo-bodies, which have been prepared by us in connection with this work.

The number of mixed azo-bodies, *i. e.*, those containing an aliphatic and an aromatic radical, is quite limited. A few have been prepared by E. Fischer and Ehrhard,<sup>3</sup> and Tafel<sup>4</sup> by the oxidation of the corresponding hydrazo-derivatives. The principal method of preparation is, however, by combining aromatic diazo-salts with aliphatic compounds. This reaction, first worked out by V. Meyer<sup>5</sup> on nitroethane, has since been extended to a large number of such aliphatic compounds, as contain a (CH<sub>2</sub>)<sub>n</sub>-group linked to some negative groups. Nitro-compounds, malonic ester, aceto-acetic ester, etc., give such bodies. The constitution of all these so-called azo-bodies has, however, recently been called into question by the work of Japp

<sup>1</sup> Read at the Boston meeting of the American Chemical Society, August, 1898.

<sup>2</sup> *Ber. d. chem. Ges.*, 30, 2043; *This Journal*, 20, 773.

<sup>3</sup> *Ann. Chem. (Liebig)*, 199, 328, 1879; *Ber. d. chem. Ges.*, 29, 793, 1896.

<sup>4</sup> *Ber. d. chem. Ges.*, 18, 1742, 1885.

<sup>5</sup> *Ber. d. chem. Ges.*, 8, 751, 1875; 18, 1742, 1885.

and Klingmann,<sup>1</sup> and others,<sup>2</sup> who have shown, for many compounds, the identity of the azo-formula,  $R.N : N.CH$ , with that of the hydrazo-formula,  $R.NHN : C$ . This has opened the

question, as to whether all the mixed azo-compounds, obtained by the above reaction, are not after all hydrazones. An intramolecular change of this nature can, of course, take place only in such compounds as contain a  $(CH)$ - or  $(CH_2)$ -group. If this view be correct, then the number of mixed azo-bodies is indeed very small. The phenylazoisovaleric acid of Prentice<sup>3</sup> might be mentioned in this connection as being a true mixed azo-compound.

We have found that the reaction of phenylhydrazine with triphenylbrommethane is of general application. All hydrazines, so far as tried, react very readily with this bromine compound, and give hydrazo-bodies, which furnish, on oxidation, with more or less readiness, the desired azo-derivatives. The following hydrazines have been tried: Paratoluyldiazine, orthonitrophenylhydrazine, metanitrophenylhydrazine, paranitrophenylhydrazine, metachlorphenylhydrazine, parachlorphenylhydrazine, metabromphenylhydrazine, and  $\alpha$ -naphthylhydrazine.

These hydrazo-bodies are well crystallized; they are colorless, with the exception of those containing the nitro-group, which are colored yellow to reddish-brown. They are soluble in benzene, chloroform, less soluble in ether and alcohol, and very sparingly soluble in ligroin. They oxidize very readily on exposure to the air, thus resembling more the aromatic than the purely fatty hydrazo-bodies. They are weak bases and form salts with dry hydrochloric, oxalic, picric, and other acids.

The azo-derivatives are also well crystallized compounds, colored from yellow to orange. They are very soluble in benzene and chloroform, less soluble in ether, alcohol, and acetic acid, and only sparingly soluble in ligroin. They all give off their

<sup>1</sup> *Ber. d. chem. Ges.*, 20, 3398, 1887; *Ann. Chem. (Liebig)*, 247, 190.

<sup>2</sup> R. Meyer: *Ber. d. chem. Ges.*, 21, 118, 1888; 24, 1241, 1891; V. Meyer, 1888: *Ber. d. chem. Ges.*, 21, 11; Baeyer and Claisen: *Ibid.*, 1697; 25, 746, 1892; v. Pechmann, 1892: *Ber. d. chem. Ges.*, 25, 3190.

<sup>3</sup> *Ann. Chem. (Liebig)*, 292, 272.

nitrogen on being heated, thus resembling the simple triphenylmethaneazobenzene. The liberation of nitrogen is quantitative, and takes place at temperatures ranging from 103.5° to 118.5° C. The relative position of the chlorine or the nitro-group seems to exert no particular influence upon the temperature at which the azo-body decomposes.

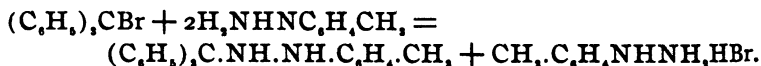
Molecular weight determinations show them to be monomolecular.

When dissolved in chloroform and treated with bromine, they form crystalline perbromides. These have not yet been analyzed.

### EXPERIMENTAL PART.

#### ACTION OF PARATOLUYLHYDRAZINE.

*Triphenylmethanehydrazoparatoluene*,  $(C_6H_5)_3C.NH.NH.C_6H_4.CH_3$ .—Paratoluyldiazine<sup>1</sup> (two molecules) was dissolved in dry ether and slowly added, with stirring, to a cold ethereal solution of triphenylbrommethane (one molecule). The solution was allowed to stand protected from the air until the precipitate of toluyldiazine hydrobromide separated out. The reaction is represented by the following equation :



Upon filtering off the precipitate of toluyldiazine hydrobromide and concentrating the ethereal solution, white crystals of the hydrazo-body were obtained. They were recrystallized from ether and analyzed with the following results :

0.212 gram gave 15 cc. nitrogen at 20° and 736.6 mm.

	Calculated for $C_{26}H_{27}N_3$ .	Found.
N .....	7.69	8.02

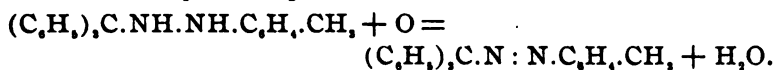
This hydrazo-derivative is readily oxidized on exposure to the air, especially in an alcoholic solution. It is a weak base, forming salts with dry hydrochloric, oxalic, picric, and other acids. It is soluble in benzene, chloroform, less soluble in alcohol and ether, and insoluble in water and ligroin. It melts with decomposition at 157° C.

*Triphenylmethaneazoparatoluene*,  $(C_6H_5)_3C.N:N.C_6H_4.CH_3$ .—After trying numerous oxidizing agents, such as potassium per-

<sup>1</sup> E. Fischer, 1876: *Ber. d. chem. Ges.*, 9, 890.



manganate, ferric chloride, mercuric oxide, and amyl nitrite, the last named reagent was found to give the best results.<sup>1</sup> The hydrazo-body was suspended in ether and the calculated quantity of amyl nitrite added. A drop of acetyl chloride was sufficient to start the action. The hydrazo-body was gradually changed to the azo, which dissolving in the ether produced a deep yellow solution. Upon concentration, long yellow needles of the azo-compound separated. The reaction is as follows:



Recrystallized from methyl alcohol the compound gave the following results upon analysis:

0.1505 gram gave 0.4725 gram carbon dioxide + 0.083 gram of water.

0.263 gram gave 18 cc. nitrogen at 21° and 731.5 mm. when heated to 150° C.

	Calculated for $C_{28}H_{22}N_2$ .	Found.
C.....	86.18	85.79
H.....	6.07	6.15
N.....	7.73	7.70

The molecular weight determination furnished the following results:

Triphenylmethaneazoparatoluene,  $C_{28}H_{22}N_2 = 362$ .

Solvent: Benzene.

Grams solvent.	Grams substance.	Observed depression.	Molecular weight found.
18.589	0.4563	0.42°	292

The azo-compound is soluble in benzene, chloroform, ether, less soluble in alcohol, and only sparingly soluble in ligroin. It melts at 103.5° C. with evolution of nitrogen. An attempt has been made to determine the products of decomposition. The substance was mixed with copper-bronze, to facilitate decomposition, and heated to 120° C. The reaction which took place was apparently a complicated one, and as yet satisfactory results have not been obtained.

#### ACTION OF NITROHYDRAZINES.

*Triphenylmethanehydrazoonitrobenzene*,  $(C_6H_5)_3C.NH.NH.-$

<sup>1</sup> Recent experiments show that nitrous acid gas, passed into an ethereal solution of the hydrazo-derivatives of triphenylmethane, gives the best results in oxidizing them to the corresponding azo-compounds. This Journal, 20, 775.

$C_6H_5NO_2(o)$ .—Orthonitrophenylhydrazine<sup>1</sup> was allowed to react with triphenylbrommethane under conditions similar to those in the preparation of triphenylmethanehydrazoparatoluene. Upon concentrating the ethereal solution brownish crystals of triphenylmethanehydrazoorthonitrobenzene separated. The yield is quantitative. Recrystallized from ether it was analyzed with results as follows:

0.1816 gram gave 17.4 cc. nitrogen at 22.5° and 741.7 mm.

	Calculated for $C_{18}H_{15}N_3O_2$ .	Found.
N .....	10.63	10.86

This hydrazo-compound is soluble in benzene, chloroform, less soluble in ether and alcohol, and is insoluble in ligroin. It forms salts with dry acids, melting-point 168° C. It oxidizes partially to the azo-compound on exposure to the air.

*Triphenylmethaneazoorthonitrobenzene*,  $(C_6H_5)_3C.N:N.C_6H_4NO_2(o)$ .—This compound is prepared from the corresponding hydrazo-body by oxidation with amyl nitrite or nitrous acid gas in an ethereal solution. Recrystallized from methyl alcohol it is obtained in bright canary-yellow needles, perfectly pure.

0.261 gram gave 0.7273 gram carbon dioxide + 0.1201 gram of water.

0.1437 gram gave 13.5 cc. nitrogen at 22° and 739 mm.

	Calculated for $C_{18}H_{15}N_3O_2$ .	Found.
C .....	76.33	75.98
H .....	4.83	5.11
N .....	10.67	10.62

The compound is soluble in benzene, chloroform, ether less soluble in alcohol, and sparingly soluble in ligroin. Melting-point 116° C. It forms a crystalline perbromide.

Molecular weight determination:

Triphenylmethaneazonitrobenzene,  $C_{18}H_{15}N_3O_2 = 393$ .

Solvent: Benzene.

Grams solvent.	Grams substance.	Observed depression.	Molecular weight found.
18.598	0.6245	0.49°	338

*Triphenylmethanehydrazometanitrobenzene*,  $(C_6H_5)_3C.NH.NH.C_6H_4NO_2(m)$ .—Metanitrophenylhydrazine<sup>2</sup> is treated with triphenylbrommethane, as in the case of the corresponding ortho-

<sup>1</sup> Bischler, 1889: *Ber. d. chem. Ges.*, 22, 2801.

<sup>2</sup> Bischler and Brodsky, 1889: *Ber. d. chem. Ges.*, 22, 2809.

body. The hydrazo-compound crystallizes out on concentrating the solution in reddish-brown crystals. Recrystallized from ether it gave the following results:

0.2374 gram gave 0.6528 gram carbon dioxide + 0.1151 gram of water.

0.2342 gram gave 22.6 cc. nitrogen at 22° and 741.7 mm.

	Calculated for $C_{18}H_{11}N_3O_2$ .	Found.
C.....	75.37	75.11
H.....	5.28	5.34
N.....	10.63	10.96

The body is soluble in benzene, chloroform, less soluble in ether and alcohol, and very sparingly soluble in ligroin, melting-point 165° C. Yield quantitative.

*Triphenylmethaneazometanitrobenzene*,  $(C_6H_5)_3C.N:N.C_6H_4NO_2$ -(*m*), is prepared by oxidation of the corresponding hydrazo-body. Recrystallized from methyl alcohol it forms canary-yellow needles.

0.2535 gram gave 22.5 cc. nitrogen at 23.5° and 734 mm.

	Calculated for $C_{18}H_{11}N_3O_2$ .	Found.
N.....	10.67	9.98

The azo-compound is soluble in ether, benzene, less soluble in alcohol, and sparingly soluble in ligroin, melting-point 111°–112° C. It forms a crystalline perbromide.

Triphenylmethaneazonitrobenzene,  $C_{18}H_{11}N_3O_2 = 393$ .

Solvent: Benzene.

Grams solvent.	Grams substance.	Observed depression.	Molecular weight found.
16.874	0.556	0.46°	361

*Triphenylmethanehydrazoparanitrobenzene*,  $(C_6H_5)_3C.NH.NH.C_6H_4NO_2$ -(*p*).—Paranitrophenylhydrazine<sup>1</sup> was allowed to act on triphenylbrommethane as in previous instances. The ethereal solution was evaporated nearly to dryness, when the hydrazo body crystallized in large reddish needles. Yield almost quantitative. Recrystallized from ether it gave the following figures:

0.2163 gram gave 21.8 cc. nitrogen at 22° and 730 mm.

	Calculated for $C_{18}H_{11}N_3O_2$ .	Found.
N.....	10.63	11.15

Triphenylmethanehydrazoparanitrobenzene is very soluble in

<sup>1</sup> *Ber. d. chem. Ges.* 25, 119, Ref.

benzene, chloroform and ether, less soluble in alcohol, and sparingly soluble in ligroin. Melting-point  $170^{\circ}\text{C}$ . It is a weak base and forms salts with dry acids.

*Triphenylmethaneazoparanitrobenzene*,  $(\text{C}_6\text{H}_5)_3\text{C.N:N.C}_6\text{H}_4\text{NO}_2$  (*p*).—This body results from the oxidation of the corresponding hydrazo-compound with amyl nitrite or nitrous acid gas, and crystallizes from methyl alcohol in large reddish needles. It was analyzed with the following results:

0.1763 gram gave 17 cc. nitrogen at $24^{\circ}$ and 736.4 mm.	
Calculated for $\text{C}_{22}\text{H}_{18}\text{N}_4\text{O}_2$ .	Found.
N..... 10.67	10.76

The compound is very soluble in benzene, chloroform, ether, less soluble in alcohol, and very sparingly in ligroin. Melting-point  $118.5^{\circ}\text{C}$ . The determination of the molecular weight shows it to be monomolecular.

Triphenylmethaneazonitrobenzene,  $\text{C}_{22}\text{H}_{18}\text{N}_3\text{O}_2 = 393$ .

Solvent: Benzene.

Grams solvent.	Grams substance.	Observed depression.	Molecular weight found.
16.698	1.0965	$0.855^{\circ}$	381

#### ACTION OF CHLORHYDRAZINES.

*Metachlorphenylhydrazine*,  $\text{ClC}_6\text{H}_4\text{.NHNH}_2$ .—Ten grams of metachloraniline were dissolved in ten times its weight of concentrated hydrochloric acid and cooled with ice. The calculated quantity of sodium nitrite, dissolved in twice its weight of water, was added. The diazo-solution was then reduced with the calculated quantity of stannous chloride dissolved in strong hydrochloric acid. A white precipitate of the double hydrochloride of tin and chlorphenylhydrazine separated out. This was redissolved in boiling water, decomposed with potassium hydroxide and the free base extracted with ether. The yield is about eighty-five per cent. of the theoretical quantity. Fractionated in a vacuum, it is obtained as a colorless liquid boiling at  $165^{\circ}\text{C}$ . at 23 mm. It remains liquid at  $-15^{\circ}\text{C}$ . It gave the following figures on analysis:

0.2717 gram gave 0.2700 gram silver chloride.

0.1559 gram gave 27.7 cc. nitrogen at  $23^{\circ}$  and 739 mm.

	Calculated for $\text{C}_6\text{H}_7\text{N}_2\text{Cl}$ .	Found.
Cl.....	24.91	24.55
N.....	19.65	20.19

*Triphenylmethanehydrazometachlorbenzene*,  $(C_6H_5)_3C.NH.NH.C_6H_4Cl(m)$ .—The preparation is similar to that of the preceding hydrazo-bodies. Recrystallized from ether it gave the following results on analysis :

0.3665 gram gave 23.8 cc. nitrogen at  $21.5^\circ$  and 737 mm.

	Calculated for $C_{21}H_{21}N_3Cl$ .	Found.
N .....	7.28	7.36

It is colorless when pure, but turns yellow on exposure, due to partial oxidation. It is soluble in benzene, chloroform, less soluble in ether and alcohol, and very sparingly soluble in ligroin. It melts at  $150^\circ C$ .

*Triphenylmethaneazometachlorbenzene*,  $(C_6H_5)_3C.N : N.C_6H_4Cl(m)$ .—This body is prepared in the same way as the previous azo-bodies. Recrystallized from methyl alcohol it forms bright yellow needles.

0.2607 gram gave 0.0632 gram silver chloride.

0.2463 gram gave 17 cc. nitrogen at  $19^\circ$  and 736.6 mm.

	Calculated for $C_{21}H_{19}N_3Cl$ .	Found.
Cl .....	9.32	9.85
N .....	7.32	7.83

It is soluble in benzene, chloroform, less soluble in ether and alcohol, and is slightly soluble in ligroin. It melts at  $109^\circ C$ . The following molecular weight determination shows it to be monomolecular.

*Triphenylmethaneazochlorbenzene*,  $C_{21}H_{19}N_3Cl = 382.5$ .

Solvent : Benzene.

Grams solvent.	Grams substance.	Observed depression.	Molecular weight found.
20.700	0.6452	$0.475^\circ$	330

*Triphenylmethanehydrazoparachlorbenzene*,  $(C_6H_5)_3C.NH.NH.C_6H_4Cl(p)$ .—This is obtained by the action of parachlorhydrazine on triphenylbrommethane. Analysis gave the following figures :

0.1593 gram gave 0.0715 gram silver chloride.

0.3458 gram gave 24.2 cc. nitrogen at  $24^\circ$  and 741.7 mm.

	Calculated for $C_{21}H_{21}N_3Cl$ .	Found.
Cl .....	9.44	9.95
N .....	7.28	7.89

It melts at  $145^\circ C$ ., and in other properties resembles the corresponding chlor-derivatives closely.

*Triphenylmethaneazoparachlorbenzene*,  $(C_6H_5)_3C.N : N.C_6H_4Cl$  (*p*).—The preparation and properties of this body are similar to those of the corresponding chlorazo-body. It melts at  $107^\circ C$ .

0.142 gram heated to  $130^\circ C$ . gave 8.8 cc. nitrogen at  $23.5^\circ$  and 734 mm.

	Calculated for $C_{18}H_{15}N_2Cl$ .	Found.
N .....	7.32	6.92.

#### ACTION OF METABROMPHENYLHYDRAZINE.

*Metabromphenylhydrazine*,  $C_6H_4Br.NHNH_2$ .—This compound was prepared in the same way as the corresponding chlorhydrazine. It is a colorless liquid. Analyzed it gave the following results :

0.2672 gram gave 0.3687 gram carbon dioxide + 0.0942 gram of water.

0.1887 gram gave 25 cc. nitrogen at  $21^\circ$  and 746.8 mm.

0.4513 gram gave 58.4 cc. nitrogen at  $18.5^\circ$  and 727.7 mm.

	Calculated for $C_6H_7N_2Br$ .	I.	Found.	II.
C .....	38.50	38.29	....	....
H .....	3.74	3.91	....	....
N .....	14.97	14.54	15.12	....

When the base is treated with hydrochloric acid a chloride containing one molecule of the acid is formed.

*Triphenylmethanehydrazometabrombenzene*,  $(C_6H_5)_3C.NH.NH.C_6H_4Br$  (*m*).—Mode of preparation and properties similar to those of the corresponding chlor-compound ; melting-point  $149^\circ C$ .

0.3017 gram gave 0.7693 gram carbon dioxide + 0.1336 gram of water.

0.3000 gram gave 18.8 cc. nitrogen at  $19^\circ$  and 741.7 mm.

0.2533 gram gave 16 cc. nitrogen at  $22^\circ$  and 734 mm.

	Calculated for $C_{18}H_{21}N_2Br$ .	I.	Found.	II.
C .....	69.93	69.55	....	....
H .....	4.89	4.92	....	....
N .....	6.52	6.84	7.09	....

*Triphenylmethaneazometabrombenzene*,  $(C_6H_5)_3C.N : N.C_6H_4Br$  (*m*).—Preparation and properties similar to those of the corresponding chlor-compound ; melting-point  $110^\circ C$ . Analysis gave the following results :

0.2273 gram gave 0.5860 gram carbon dioxide + 0.1030 gram of water.

0.2606 gram gave 16.4 cc. nitrogen at 22° and 746 mm.

	Calculated for $C_{21}H_{19}N_3Br$ .	Found.
C .....	70.25	70.31
H .....	4.45	4.85
N .....	6.55	6.92

Molecular weight determination :

Triphenylmethaneazobrombenzene,  $C_{21}H_{19}N_3Br = 427$ .

Solvent: Benzene.

Grams solvent.	Grams substance.	Observed depression.	Molecular weight found.
20.800	1.1020	0.70°	378

#### ACTION OF $\alpha$ -NAPHTHYLHYDRAZINE.

*Triphenylmethanehydrazo- $\alpha$ -naphthalene*,  $(C_6H_5)_3C.NH.NH.C_{10}H_7$ , is produced when triphenylbrommethane is treated with the  $\alpha$ -naphthylhydrazine.<sup>1</sup> The ethereal solution should be evaporated in absence of air, and the crystalline residue rapidly dried, as this hydrazo-compound is very prone to oxidation, giving a dark-brown mass. The pure hydrazo-compound crystallizes in small white cubes.

0.2650 gram gave 18.2 cc. nitrogen at 21.5° and 734 mm.

	Calculated for $C_{29}H_{21}N_3$ .	Found.
N .....	7.00	7.68

It is very soluble in ether, benzene, chloroform, less soluble in alcohol, and only slightly in ligroin.

*Triphenylmethaneazo- $\alpha$ -naphthalene*,  $(C_6H_5)_3C.N:N.C_{10}H_7(\alpha)$ . —This azo-compound could not be obtained when amyl nitrite was employed. But upon careful oxidation of the hydrazo-derivative, suspended in a mixture of ether and ligroin, with nitrous acid gas, the azo-body separates out in bright yellow needles, mixed with reddish-yellow cubes. Both forms of the crystals give the same melting-point, 114° C.

0.1995 gram gave 13.6 cc. nitrogen at 22° and 730 mm.

	Calculated for $C_{29}H_{21}N_3$ .	Found.
N .....	7.03	7.61

In its general properties and solubility it resembles the other azo-derivatives of triphenylmethane.

ANN ARBOR, MICHIGAN.

<sup>1</sup> *Ann. Chem.* (Liebig), 232, 236.

## A PERIODIDE OF TRIPHENYLBROMMETHANE.<sup>1</sup>

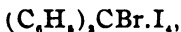
BY M. GOMBERG.

Received August 29, 1898.

IN an attempt to prepare triphenyliodomethane the corresponding bromine compound was heated with finely powdered potassium iodide suspended in benzene. The solution soon turned dark red, showing the liberation of iodine from the potassium salt. The purer the bromine compound, the less iodine was set free, while prolonged boiling, even with the purest reagents, increased its yield. The benzene solution, filtered from the potassium salts, deposited, on cooling, a small crop of bluish green iridescent crystals, resembling, in their appearance and behavior, the well-known periodides of organic bases. The crystals contained both iodine and bromine, and it was therefore concluded that their formation was due to the action of the small quantity of free iodine upon the triphenylbrommethane.

Accordingly, a solution of iodine in benzene was added to a solution of the bromine compound, also in benzene. The periodide invariably separated in the form of crystals, the size of which depended upon the concentration of the solution. These crystals proved to be identical in every respect with those obtained when potassium iodide was employed.

The periodide was found to be of the composition



with all the iodine held loosely, just as in the periodides of organic bases. The iodine could be titrated directly with standard solutions of sodium thiosulphate or sodium arsenite.

The periodide here described differs in some respects from the other compounds of this class. The formation of superperiodides has been limited, with a few exceptions, to the nitrogen family of the elements,<sup>2</sup> the largest number of such superperiodides being those of the organic nitrogen bases. Even the few exceptions are, after all, periodides of substances either themselves basic in their nature, or in combination with bases. The periodides of the diazo salts<sup>3</sup> are strictly such of bases. The superperiodides of

<sup>1</sup> Read at the Boston meeting of the American Chemical Society, August, 1898.

<sup>2</sup> Prescott, 1895 : This Journal, 17, 779.

<sup>3</sup> Hantzsch, 1895 : *Ber. d. chem. Ges.*, 28, 27 4.



iodonium salts<sup>1</sup> find their explanation in the fact that the iodonium compounds are bases in every other respect as well. The periodides of metals are such of *inorganic* bases. The sulphon periodides of Kastle and Hill<sup>2</sup> are analogous to the herapathites of Jörgensen, with substitution of an inorganic base for an organic. The periodide of triphenylbrommethane, however, has not, so far as I am aware, its analogue. It is not a periodide of a salt of a base, nor of a free base<sup>3</sup>. On the contrary, triphenylbrommethane is made up entirely of negative groups. The periodide is unlike those recently described by Remsen and Norris.<sup>4</sup> It can hardly be assumed that the iodine adds itself to any of the benzene rings in the triphenylmethane. It must be linked to the molecule through the bromine atom.

I have shown some time ago<sup>5</sup> that the amount of additive iodine (or bromine) in a base is in no way proportional to, or indicative of, the basic power of the compound. And here we have an example of a periodide, with as many as four atoms of additive iodine, of a substance which has no basic properties whatever.

*Triphenylbrommethane Tetraiodide*,  $(C_6H_5)_3CBr.I_4$ .—When a saturated benzene solution of iodine is added to a solution of triphenylbrommethane in benzene, a dark granular precipitate, soon changing to crystals, is thrown down. The periodide in this form always contains a little free iodine, which is difficult to remove by mere washing with benzene. When dilute solutions of the reagents are employed, the precipitation does not take place at once, and the solution has to be set aside for some time, or gently concentrated. Slow crystallization gives larger crystals, but these also contain frequently from two to three per cent. of free iodine. The periodide can also be obtained by substituting carbon disulphide for benzene, but in this case the solutions must be more concentrated, as the periodide is quite soluble in carbon disulphide. The amount of iodine employed varied in the different experiments from one-half to three times the theoretical quantity, but in no case was the formation

<sup>1</sup> *Ber. d. chem. Ges.*, 27, 1594.

<sup>2</sup> *Am. Chem. J.*, 16, 116.

<sup>3</sup> Such as  $C_6N_6N.I_4$ . (Prescott and Trowbridge: *This Journal*, 17, 865.)

<sup>4</sup> *Am. Chem. J.*, 18, 94, 1896.

<sup>5</sup> *This Journal*, 18, 377.

of either a higher or a lower periodide observed than the one here described. The yield is very good. When benzene is employed as a solvent, eighty to eighty-five per cent. of the theoretical quantity of the periodide is obtained.

For analysis, the periodide was recrystallized from warm benzene or carbon disulphide. The crystals were filtered off by means of a pump, washed with a little benzene, and dried, *in vacuo*, over sulphuric acid. The iodine was estimated in most cases by titrating weighed samples of the substance suspended in alcohol with a sodium thiosulphate solution. In some cases the iodine was estimated by reducing the periodide with zinc dust and water. The iodine was set free by a saturated solution of nitrous acid in concentrated sulphuric acid, extracted with carbon disulphide, the latter washed with a weak solution of sodium carbonate, and the iodine titrated as before. The bromine was estimated by igniting the periodide with lime and estimating the total halogen, *i. e.*, bromine and iodine together, with silver nitrate solutions. From the total mixture of silver halides, the quantity of silver iodide corresponding to the amount of iodine, as found by titration, is subtracted. The difference represents silver bromide.

The following are some of the analyses obtained on different samples of the perhalide :

- I. 0.2203 gram substance gave 0.1340 gram iodine.
- II. 0.3428 gram substance gave 0.2100 gram iodine.
- III. 0.1641 gram substance gave 0.1027 gram iodine.
- IV. 0.1495 gram substance gave 0.0914 gram iodine.
- V. 0.2560 gram substance gave 0.1578 gram iodine.
- VI. 0.4256 gram substance gave 0.2621 gram iodine.
- 0.2253 gram substance gave 0.3058 gram AgI.

	Calculated for (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> CBr.I <sub>4</sub> .	I.	II.	Found. III.	IV.	V.	VI.
Iodine.....	61.05	60.83	61.26	62.58	61.50	61.64	61.58
Bromine ...	9.61	....	....	....	....	....	9.15

Estimation IV was done by previous reduction with zinc dust ; all the others by direct titration.

The periodide is of a bluish-green iridescence. It can be obtained in long hexagonal prisms, or in small needle-like crystals. In two samples, obtained by slow crystallization, the crys-

tals were hollow, the canal coinciding as nearly as could be judged with the longitudinal axis of the crystals. The exact conditions necessary for the production of such hollow crystals have not been ascertained. Only two similar cases of crystallization have been reported, so far as I could find.<sup>1</sup> The periodide is only slightly soluble in cold benzene; more freely in hot. It is quite soluble in carbon disulphide. It is decomposed by alcohol and ether. When dry, and placed in a bottle, it remains unchanged for a long time; but when exposed to the air it gradually loses iodine. It melts at  $121^{\circ}$ – $122^{\circ}$  C.

A sample was gently heated at  $40^{\circ}$ – $45^{\circ}$  C. for some time, until the color changed to a dark gray. The residue was recrystallized from petroleum ether, and by its melting-point ( $152^{\circ}$  C.) and all other properties was identified as bromtriphenylmethane.

Attempts to determine the molecular weight by the cryoscopic method did not give satisfactory results.

I wish to thank Mr. W. H. Hess, who kindly helped me in this work.

ANN ARBOR, MICHIGAN.

## NITRIC NITROGEN PRODUCED BY THE PEA.

BY J. L. BERSON.

Received August 15, 1898.

IT has been long known that the leguminous plants contain more nitrogen than they get from the soil, hence their almost universal use as soil improvers.

Hellriegel and Wilfarth in 1886 showed that the leguminosæ would not grow in sterilized sand for lack of nitrogen, but that if the sand be inoculated with water, in which the roots of a well developed plant of the variety experimented on had been soaked, the plant would at once begin to grow, rapidly developing root tubercles. Microscopic investigation showed the presence of bacteria in these tubercles. These micro-organisms are now cultivated and sold under the name of "Nitragin" for the purpose of inoculating sterile soils, that is, soils which do not contain the leguminous micro-organisms.

Later experiments have shown that each kind of leguminous plant has its own kind of bacteria, and that those from another leguminous plant will not answer for inoculation purposes.

<sup>1</sup> Kebler, 1895: *Am. J. Pharm.*, 67, 602; Trowbridge, 1897: *This Journal*, 19, 328.

The bacteria live upon the juices of the host, and in turn supply the plant with nitric nitrogen assimilated from the air in the soil, thus establishing a symbiosis. While the roots of all the leguminosæ show rather large quantities of nitric nitrogen, the question whether these bacteria furnish all the plant needs or more, has not been determined, so far as I know. If the micro-organisms should produce more nitric nitrogen than the plant needs for its growth, will not this excess help to feed a crop growing among the leguminosæ? In order to answer these questions small plots of ground of uniform character were planted in peas, peas and corn, corn, cotton and sorghum, and one plot was cultivated like the planted plots, and kept free from vegetation. Since soils produce nitrates by nitrification, and by the fixation of nitrogen from the atmosphere by means of soil bacteria, this "fallow" plot was the zero point for the measurement of the nitric nitrogen in the soil of the plots that were planted.

The soil was a rich bottom land and very productive. The analyses were made September 30, after about six weeks of dry weather. This would allow the nitrates to accumulate, if formed in excess by the pea plants.

One kilogram of soil was taken about one foot from the plants, in several places, but towards the center of each plot. It was shaken for six hours with one liter of water, the suspended clay precipitated with five grams of sodium chloride, one-half liter decanted, evaporated to small bulk, and the nitric nitrogen estimated in duplicate by the Tiemann and Schulze method. The number of milligrams of nitric nitrogen in one kilo of soil is given for each plot below.

	Nitrogen. Mgms.
Fallow plot gave.....	1.01
Peas, growing, pods nearly grown.....	3.333
Peas, growing, pods about ripe.....	8.670
Peas, grown and dead two or three weeks.....	10.510
Corn (hard), peas same as above.....	7.503
Corn (hard).....	0.340
Cotton, growing.....	0.423
Sorghum, growing.....	0.333

As was to be expected, practically no nitrates were found in

the soil under the growing cotton and sorghum. But more nitrates were found under the growing peas than under the fallow plot, showing that the micro-organisms on the pea roots assimilate more nitrogen than the plant needs for its growth, and that this excess is found in the soil. With the ripening of the peas the excess of nitrates increased, indicating a continuance of the activity of the micro-organisms until the plant has ceased to grow. It may be that they continue to grow and assimilate nitrogen after the pea plant is dead—as long as there are juices in the plant. The larger quantities of nitric nitrogen in the soil where the peas were dead, over that where the pods were ripe, would tend to show this. But the bacteriologist only can answer this question. The fact that the corn and peas plot showed less nitrates than the pea plot of the same age, yet more than the fallow plot, shows that the growing corn had used some of the nitrates in its growth. Had the corn been growing at the time the samples were taken, there would doubtless have been found still less nitrates, as the "corn" plot, though the corn was about dead, showed practically no nitrates. This excess of nitrates in the corn and pea plot was therefore likely produced largely after the corn had ceased to grow.

These experiments indicate that peas planted with a crop would tend to increase the yield of that crop, unless the peas be so thick as to interfere with the crop's root development, or use up too much water in their growth.

Whether these results will hold good for all leguminosæ, or for peas in all kinds of seasons, only further investigations can determine. It is to be hoped that the agricultural chemists of the various experiment stations will take up this very important line of work.

GEORGIA NORMAL AND INDUSTRIAL COLLEGE.

## PETROLEUM INCLUSION IN QUARTZ CRYSTALS.<sup>1</sup>

BY CHAS. L. REESE.

Received August 29, 1898.

THE quartz crystals, of which an illustration is here given, are of interest on account of the size of the cavities and the quantity and character of the liquid in them.

<sup>1</sup> Read at the Boston meeting of the American Chemical Society, August, 1898.

Sir Humphry Davy,<sup>1</sup> in a study of the fluid contents of cavities in rocks, mentions a single instance in which mineral naphtha was found in a quartz cavity.

A. W. Wright<sup>2</sup> subjected smoky quartz from Branchville, Conn., to dry distillation, and obtained a bituminous material which probably came from microscopic cavities found in the crystals, and Foster<sup>3</sup> obtained a brownish liquid, which contained ammonium carbonate, by distilling smoky quartz.

I have had these crystals in my possession for a number of years and photographed them for the purpose of publishing an account of them, but have only recently been able to obtain definitely the locality from which they came. They were found at Diamond Post-Office, near Guntersville, Marshall Co., Alabama, near the Tennessee line.

The crystals are well developed, especially No. 2, and are perfectly transparent. No. 1 measures 23.6 mm. in length and twelve mm. in width, and No. 2 measures 13.5 mm. by 9.5 mm.

The globule in No. 1, marked *A*, measures two and three-tenths mm. through its longest diameter, by one and eight-tenths mm. through its shortest diameter, and about one mm. thick. The cavity in which *A* occurs is triangular in shape with sides and edges running parallel to the rhombohedral faces and edges and, as far as it can be measured, is about one millimeter deep; its sides measuring about six mm. by five mm. by five mm.

On heating No. 1, the globule *A* broke and the oil wet the sides and edges of the cavity so that it now lies about the walls of the cavity with a globular space in the center, and can be seen to move about when the crystal is turned from side to side. Globule *B* in No. 1 also broke when the crystal was heated and also spread itself about the cavity. The heating was done in water and the breaking of the globule was accompanied by quite an explosion, which caused my removing the crystal from the source of heat for fear of shattering the specimen.

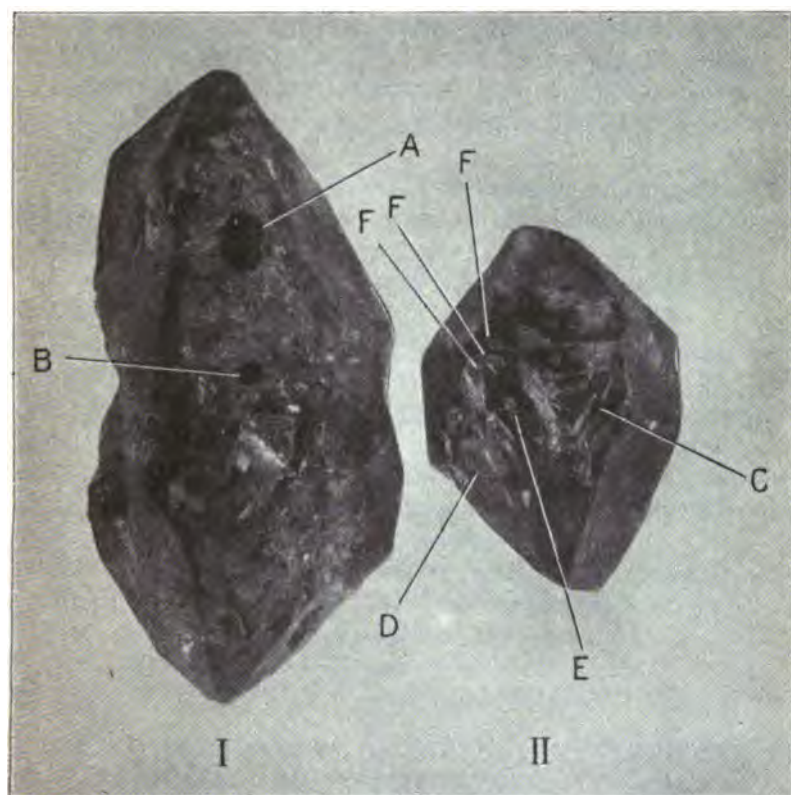
There are other cavities in No. 1 containing oil, but they do not appear distinctly in the photograph.

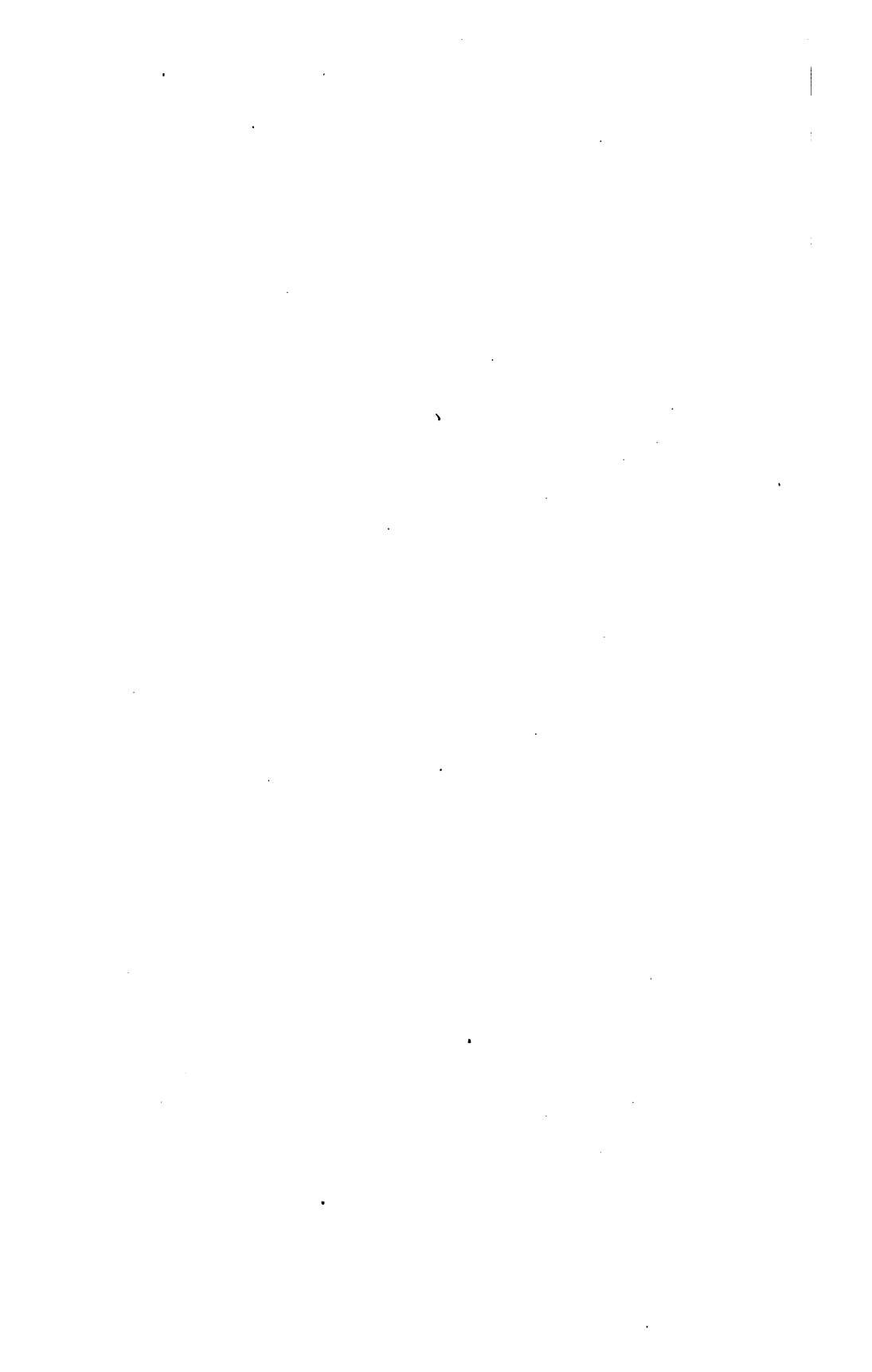
In No. 2, the two larger cavities indicated in the figure by *C*

<sup>1</sup> *Phil. Trans.*, 1822, 367.

<sup>2</sup> *Am. J. Sci.*, 21, 209, 1881.

<sup>3</sup> *Pogg. Ann.*, 143, 173.







and *D*, are also triangular in shape, with edges parallel to the rhombohedral edges, and measure respectively, *C* four and five-tenths mm. by four and five-tenths by three mm., and for *D* three by three by two mm., both about five-tenths mm. thick.

These two cavities also contain oil with a globular space in the center, which can be seen to move about when the crystal is turned.

The cavities *E* and *F*, *F*, *F*, are quite small, but can be readily seen by the naked eye, and are full of oil with the exception of a minute globule of gas.

*F*, *F*, and *F* are the same cavity, being seen by refraction from the three faces.

The evidence of the character of the oil is not chemical, but yet sufficient to identify it.

It presents the appearance of petroleum in that it has the yellow green fluorescence. Some crystals from the same source were crushed in filter-paper, and the paper having absorbed the oil, showed the grease spot and gave the characteristic odor of petroleum and burned with a smoky flame.

Another evidence of the nature of the liquid is that petroleum occurs in the neighborhood where the crystals were found.

The specific gravity of crystal No. 2 is 2.6123.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,  
No. 31.]

## I. METAL SEPARATION BY MEANS OF HYDROBROMIC ACID GAS. II. INDIUM IN TUNGSTEN MIN- ERALS.<sup>1</sup>

BY ELIZABETH ALLEN ATKINSON.

Received September 2, 1898.

### INTRODUCTION.

THE application of hydrochloric acid gas as a means of separating metals has proved very successful. By means of this agent Moyer<sup>2</sup> volatilized the oxides of bismuth and antimony completely, separating bismuth from lead and copper, and antimony from copper and lead. In addition, this mode of analysis afforded him separations of arsenic from copper, lead, cadmium, silver, cobalt, and nickel.

<sup>1</sup> From author's thesis presented for the degree of Doctor of Philosophy.

<sup>2</sup> This Journal, 18, 1029; Thesis.

Hibbs<sup>1</sup> had previously separated arsenic acid from phosphoric acid and tungstic acid, as well as molybdic acid from phosphoric acid, while Smith and Meyer,<sup>2</sup> in studying the action of haloid acids in gas form upon the salts of the elements of Group V, had observed many interesting facts, of which some have already been utilized in effecting separations, while others still remain for development.

It is natural to suppose that in these cases, when hydrochloric acid has been shown to be an effective and satisfactory separating agent, if it be replaced by hydrobromic acid gas, or any haloid acid gas, the results can almost be predicted. However, experiment alone can demonstrate the correctness or falsity of this assumption. To that end the experiments recorded in the following pages were instituted and carried out along lines almost exactly like those followed by Moyer<sup>3</sup> in order that a fair comparison could be made.

Meyer and Smith<sup>4</sup> had noticed that hydrobromic acid gas expelled arsenic and vanadic acids from their salts. Kelley and Smith<sup>5</sup> found that arsenic in the form of sulphide was also decomposed and volatilized in an atmosphere of hydrobromic acid gas. Antimony sulphide behaved similarly. It would be interesting to subject other metallic sulphides to this reagent, for it is very probable that some of them would be volatilized as readily as happens when they are exposed to heated hydrochloric acid gas. In this latter way, Smith and Field<sup>6</sup> succeeded in separating arsenic from vanadium, thus obtaining a most accurate and satisfactory mode of separating these two metals.

### I. METHOD OF WORK.

Hydrobromic acid gas was generated by dropping bromine from a separatory funnel on anthracene contained in a liter flask. Five drops a minute will give a good steady flow of the gas. The flask was placed on a water-bath in which the water was kept very near to the boiling-point.

The gas was passed through a tube containing anthracene, to

<sup>1</sup> This Journal, 17, 632.

<sup>2</sup> *Ibid.*, 17, 735.

<sup>3</sup> *Loc. cit.*

<sup>4</sup> *Loc. cit.*

<sup>5</sup> This Journal, 18, 1096.

<sup>6</sup> *Ibid.*, 18, 1051.

absorb any bromine that might be carried over, and then through a calcium-chloride tube, for absorption of moisture.

The substance to be acted upon was weighed out in a porcelain boat and placed in a combustion tube, which had been thoroughly dried. This tube was connected with the receiver by a bent tube provided with a stop-cock, which is necessary, as when the heat is removed there is danger of backward suction. The volatile substances were collected in water, with the exception of arsenic, in which case dilute nitric acid was used. The heat was obtained from a series of three fish-tail burners.

#### PREPARATION OF ANTIMONY TRIOXIDE.

Metallic antimony was ground in a mortar and treated with dilute nitric acid. The resulting metantimonic acid was dissolved in hydrochloric acid, and the oxychloride precipitated by an excess of water, washed thoroughly by decantation, dissolved in hydrochloric acid, and again precipitated. This procedure was repeated several times, and finally the antimony was precipitated by ammonium carbonate, filtered, washed, dried, and ignited to constant weight.

#### ACTION OF HYDROBROMIC ACID GAS ON ANTIMONY TRIOXIDE.

A slow current of the gas was passed over the oxide for one hour and a half. The first fifteen minutes in the cold; for an hour by heat given from a flame a half inch high, from three fish-tail burners placed two inches below the tube resting in an iron gutter.

At the end of the hour all the antimony had volatilized. The gas was then passed fifteen minutes in the cold, to insure the expulsion of all the volatilized bromide.

In the first experiments the tube containing the boat with the substance was run through holes in the ends of a drying oven. This oven was heated by means of a Bunsen burner. This method of heating had the advantage over that in which a direct flame was used, in that the exact temperature could be noticed by means of a thermometer.

After various experiments, I found it more satisfactory to be able to watch the reaction. The flow of gas and the heat could then be regulated so that the most satisfactory results could be obtained.

The volatilization of the antimony bromide could be somewhat hurried if a more rapid current of the gas was used, and a higher temperature allowed, but in view of the fact that this method was to be used as a means of separation from bromides of other metals that were slightly volatile at a high heat, I followed the above conditions.

#### PREPARATION OF LEAD OXIDE.

Pure lead acetate was ignited; the residue was dissolved in nitric acid, evaporated to dryness, and ignited to constant weight.

#### ACTION OF HYDROBROMIC ACID GAS ON LEAD OXIDE.

Hydrobromic acid gas was passed over the oxide for two hours, using a slightly higher temperature than with the antimony. The tubes were washed into the receiver and the tests made for lead. It was not present, proving that lead had not volatilized.

An amount by weight of the oxide was treated as above. After allowing it to cool in an atmosphere of the gas, the boat and its contents were removed to a desiccator, and after standing a half hour they were weighed.

The results indicated that the residue remaining in the boat was not lead bromide, but evidently a mixture of lead oxide and bromide. The boat and its contents were returned to the tube, and the reaction with the gas continued for one hour, when the boat was allowed to cool, and again weighed. It had gained in weight, indicating that more of the oxide had been changed into bromide. This led me to suppose that if the action of the gas was continued long enough all the oxide could be converted into bromide. This proved to be erroneous, as the weights taken after the substance had been exposed to the gas for four hours and for five hours were the same.

The following series of seven results seem to show that the compound obtained has the formula  $\text{PbO}_{.5}\text{PbBr}_2$ :

Experiment.	PbO taken. Gram.	PbO. <sub>5</sub> PbBr <sub>3</sub> obtained. Gram.	PbO. <sub>5</sub> PbBr <sub>3</sub> required. Gram.	Difference. Gram.
1.....	0.1059	0.1626	0.1624	0.0002
2.....	0.1209	0.1862	0.1859	0.0003
3.....	0.1314	0.2029	0.2016	0.0013
4.....	0.1649	0.2534	0.2530	0.0004
5.....	0.2046	0.3150	0.3139	0.0011
6.....	0.1475	0.2270	0.2263	0.0007
7.....	0.1145	0.1747	0.1756	0.0009

Moyer's experiments with hydrochloric acid gas on lead oxide indicated that all the oxide changed completely into chloride, in the cold, in two hours, and that this chloride slightly volatilized at a temperature above 225°. His chloride completely dissolved in hot water. My compound, on treatment with hot water, left a small black residue.

#### THE SEPARATION OF ANTIMONY FROM LEAD.

The oxides were thoroughly mixed in a boat and the hydrobromic acid gas passed over them for one hour and a half. The same conditions were observed as when antimony was treated alone.

In experiments 1 and 2 the antimony was estimated as oxide; in the third experiment as sulphide.

Experiment.	Sb <sub>2</sub> O <sub>3</sub> taken. Gram.	Sb <sub>2</sub> O <sub>3</sub> found. Gram.	Difference. Gram.
1.....	0.1248	0.1248	0.0000
2.....	0.1042	0.1032	0.0012
3.....	0.1180	0.1174	0.0006

In the third experiment the treatment with the gas was continued until a constant weight was obtained for the residue in the boat. The compound which resulted corresponded to the formula PbO.<sub>5</sub>PbBr<sub>3</sub>.

Experiment.	PbO taken. Gram.	PbO. <sub>5</sub> PbBr <sub>3</sub> obtained. Gram.	PbO. <sub>5</sub> PbBr <sub>3</sub> required. Gram.	Difference. Gram.
1.....	0.1180	0.1808	0.1813	0.0005

In the other two experiments compounds were obtained that did not even approximate any definite formula.

By this method a clean separation of antimony from lead may be effected.

## PREPARATION OF BISMUTH OXIDE.

Commercially pure bismuth nitrate was dissolved in nitric acid and the oxynitrate precipitated by an excess of water, washed by decantation, filtered, dissolved in nitric acid, and reprecipitated by water. This operation was repeated several times. Finally the oxide was dissolved in nitric acid and precipitated with ammonium hydroxide and ammonium carbonate from a boiling solution. The basic carbonate, ignited to constant weight, gave pure bismuth trioxide.

## ACTION OF HYDROBROMIC ACID GAS ON BISMUTH TRIOXIDE.

Hydrobromic acid gas was passed over a weighed amount of bismuth oxide for two hours and a half, the first thirty minutes in the cold; it was then gradually heated until the last half hour, during which time a flame was used from a fish-tail burner a half inch high, placed two inches below the tube.

The bismuth bromide was not so volatile as the antimony salt, but at the end of two hours and a half it was all volatilized if the above conditions had been observed. It first sublimed above the boat and could then be easily driven out of the tube.

The bismuth collected in the receiver was evaporated to dryness, taken up with nitric acid, and placed in a weighed crucible, when the solution was evaporated to dryness and taken up with nitric acid. This operation must be repeated several times, or the oxybromide which may be formed, is not entirely broken up. It was finally weighed as bismuth trioxide.

The following results were obtained :

Experiment.	$\text{Bi}_2\text{O}_3$ taken. Gram.	$\text{Bi}_2\text{O}_3$ found. Gram.	Difference. Gram.
1 .....	0.1954	0.1954	0.0000
2 .....	0.1575	0.1577	0.0002
3 .....	0.1529	0.1534	0.0005

## THE SEPARATION OF BISMUTH FROM LEAD.

The two oxides were thoroughly mixed in a porcelain boat. The hydrobromic acid gas was passed over them for two hours and a half. The same conditions were maintained as for the volatilization of the bismuth alone.

The following results were obtained :

Experiment.	$\text{Bi}_2\text{O}_3$ taken. Gram.	$\text{Bi}_2\text{O}_3$ found. Gram.	Difference. Gram.
1 .....	0.1002	0.1006	0.0004
2 .....	0.1356	0.1360	0.0004

The lead compound in the boat contained no bismuth, and the volatile sublimate showed, on appropriate tests, that lead was absent.

This separation cannot be carried out as rapidly as the separation of antimony from lead, owing to the less volatility of bismuth.

Moyer met difficulties in the separation of bismuth from lead by means of hydrochloric acid gas, owing to the fact that a little of the lead chloride volatilized at a temperature as low as  $180^\circ$ .

In the experiments with hydrobromic acid gas, I did not notice that any of the lead volatilized at a temperature necessary to volatilize the bismuth, but a slow current of the gas was best, as otherwise some of the lead was mechanically driven out with the bismuth.

Moyer found that it took from seven to eight hours to volatilize all of the bismuth by means of hydrochloric acid gas. My results show that it can be done with hydrobromic acid gas in two hours and a half.

The residue in the boat was weighed, but in no case did it correspond to a definite compound.

#### THE PREPARATION OF COPPER OXIDE.

Copper nitrate was recrystallized several times, and was then ignited to constant weight.

#### ACTION OF HYDROBROMIC ACID GAS ON COPPER OXIDE.

The hydrobromic acid gas was passed over the pure, black oxide for two and one-half hours, the same conditions being observed as with bismuth. On testing the contents of the receiver, copper was found to be absent.

#### SEPARATION OF BISMUTH FROM COPPER.

Pure bismuth oxide and copper oxide were weighed and thoroughly mixed, and then exposed to the action of hydrobromic acid gas for two and one-half hours. The conditions noted under bismuth were observed here.

The volatile bismuth bromide was collected in a receiver containing water and estimated by the method already described.

The copper compound remaining in the boat had various colors, always green when hot and usually grayish white when cold; but its weight, whatever its color, always corresponded to the formula  $\text{CuBr}$ . The compound held tenaciously to hydrobromic acid gas, so it was necessary to allow it to stand over soda-lime for at least forty-five minutes before weighing. The first few experiments gave varying results, because the heat used was too low, and the major part of the copper compound remained as cupric bromide in beautiful iodine-like crystals; but when sufficient heat was applied to volatilize all of the bismuth, the higher copper bromide was decomposed, the bromine coming off in clouds.

Moyer found that at the temperature necessary to volatilize bismuth chloride the cupric chloride was not decomposed, and that it could be weighed directly as that salt.

The following results were obtained, using this method of separation :

Experiment.	$\text{Bi}_2\text{O}_3$ taken. Gram.	$\text{Bi}_2\text{O}_3$ found. Gram.	Difference. Gram.
1 .....	0.1273	0.1277	0.0004
2 .....	0.1111	0.1121	0.0010
3 .....	0.1162	0.1170	0.0008

Experiment.	$\text{CuO}$ taken. Gram.	$\text{CuBr}$ found. Gram.	$\text{CuBr}$ required. Gram.	Difference. Gram.
1 .....	0.1103	0.2010	0.1996	0.0014
2 .....	0.1318	0.2385	0.2394	0.0009

#### SEPARATION OF ANTIMONY FROM COPPER.

The same material was used as in the preceding experiments. The weighed oxides were thoroughly mixed. The antimony bromide was completely volatilized in one and a half hours, leaving cuprous bromide in the boat. The same care was exercised as in the separation of bismuth from copper, to insure the decomposition of the cupric bromide to cuprous bromide.

The volatile antimony bromide was collected in water.

At the close of the reaction the tubes and bulb were washed out with acidulated water, and the antimony precipitated with hydrogen sulphide water. The antimony sulphide was then fil-



tered through a tared filter, the precipitate washed with alcohol, with carbon disulphide, again with alcohol, and finally with a mixture of alcohol and ether. It was then dried at from  $105^{\circ}$  to  $110^{\circ}$  in the air-bath, and weighed. The copper was weighed as cuprous bromide.

This bromide, as before mentioned, had various colors, running from a light gray through yellow and green to almost a black.

The copper bromide obtained contained no antimony, and the volatile antimony compound was entirely free from copper.

Experiment.	CuO taken. Gram.	CuBr found. Gram.	CuBr required. Gram.	Difference. Gram.
1.....	0.1025	0.1853	0.1855	0.0002
2.....	0.1218	0.2210	0.2204	0.0006
3.....	0.1137	0.2059	0.2058	0.0001

Experiment.	Sb <sub>2</sub> O <sub>3</sub> taken. Gram.	Sb <sub>2</sub> S <sub>3</sub> found. Gram.	Sb <sub>2</sub> S <sub>3</sub> required. Gram.	Difference. Gram.
1.....	0.1250	0.1465	0.1458	0.0007
2.....	0.1181	0.1385	0.1377	0.0008

#### PREPARATION OF COPPER ARSENATE.

Commercial, chemically pure sodium arsenate was recrystallized three times and then gently ignited for one hour. Pyroarsenate resulted. Copper sulphate was recrystallized three times. A solution of this salt was mixed with a solution of the pure pyroarsenate, when green copper arsenate was precipitated. It was washed repeatedly and dried in an air-bath at  $100^{\circ}$ .

Salkowski<sup>1</sup> states that copper arsenate still contains water above  $130^{\circ}$ . Moyer worked with a salt with the composition  $\text{Cu}_3\text{As}_2\text{O}_{11} \cdot 2\text{H}_2\text{O}$ . My salt prepared by the same method had the same composition.

#### SEPARATION OF ARSENIC FROM COPPER.

The weighed copper arsenate was exposed to the action of the hydrobromic acid gas for two hours—fifteen minutes in the cold, one hour with the flame of three fish-tail burners a quarter of an inch high, a half an hour with flame an inch high from the same burners, and finally fifteen minutes in the cold.

The arsenic and water were driven out at the low heat. Higher heat decomposed the cupric bromide into cuprous bro-

<sup>1</sup> *J. prakt. Chem.*, 104, 124.

mide and bromine. The cuprous bromide may be weighed in that condition after it has stood over soda-lime for forty-five minutes. Its color varied as it did in the other experiments already described.

The arsenic was washed out of the bulb into a beaker, warmed with nitric acid to insure oxidation, and precipitated from an ammoniacal solution with a magnesium solution. It was finally weighed as magnesium pyroarsenate.

The results follow :

Experiment.	$\text{Cu}_3\text{As}_2\text{O}_8 + 2\text{H}_2\text{O}$ taken. Gram.	CuBr obtained. Gram.	CuBr required. Gram.	Difference. Gram.
1.....	0.1227	0.1054	0.1046	0.0008
2.....	0.1238	0.1051	0.1055	0.0004
3.....	0.1137	0.0958	0.0969	0.0011

Experiment.	$\text{Cu}_3\text{As}_2\text{O}_8 + 2\text{H}_2\text{O}$ taken. Gram.	$\text{Mg}_3\text{As}_2\text{O}_7$ obtained. Gram.	$\text{Mg}_3\text{As}_2\text{O}_7$ required. Gram.	Difference. Gram.
1.....	0.1238	0.0766	0.0762	0.0004

#### PREPARATION OF SILVER ARSENATE.

The pure sodium pyroarsenate prepared as before described, was precipitated with silver nitrate. The nitrate was kept in excess. The reddish brown precipitate was washed with boiling water until the filtrate ceased to show the presence of silver when tested with hydrochloric acid. The silver arsenate was dried at  $110^\circ$ .

#### SEPARATION OF ARSENIC FROM SILVER.

Hydrobromic acid gas attacked the silver arsenate in the cold, forming yellow silver bromide. In the following experiments the salt was exposed to the action of the gas for one hour and a quarter. The reaction was allowed to take place for a half hour in the cold, and for thirty minutes a low heat was used. The resulting bromide was allowed to cool in the gas. Silver was not present in the receiver, and the silver bromide also proved to be free from arsenic.

The silver bromide was weighed as such. The arsenic was estimated as magnesium pyroarsenate.

Experiment.	Ag <sub>3</sub> AsO <sub>4</sub> taken. Gram.	AgBr obtained. Gram.	AgBr required. Gram.	Difference. Gram.
1.....	0.1783	0.2174	0.2171	0.0003
2.....	0.1990	0.2429	0.2424	0.0005
3.....	0.1677	0.2050	0.2042	0.0008

Experiment.	Ag <sub>3</sub> AsO <sub>4</sub> taken. Gram.	Mg <sub>3</sub> As <sub>2</sub> O <sub>7</sub> obtained. Gram.	Mg <sub>3</sub> As <sub>2</sub> O <sub>7</sub> required. Gram.	Difference. Gram.
1.....	0.1677	0.0561	0.0561	0.0000

## PREPARATION OF CADMIUM ARSENATE.

Cadmium sulphate was recrystallized three times and then precipitated by a solution of sodium pyroarsenate. A white gelatinous salt was precipitated, which, upon stirring, became granular. The salt was washed thoroughly and dried at 110°.

Salkowski<sup>1</sup> had previously prepared this salt and observed that a red heat was necessary to completely dehydrate it. Moyer's salt contained two molecules of water. My salt also had the composition  $\text{Cd}_3\text{As}_2\text{O}_7 + 2\text{H}_2\text{O}$ .

## SEPARATION OF ARSENIC FROM CADMIUM.

The hydrobromic acid gas was passed over the arsenate for one hour and a half, the same conditions being maintained as for the silver arsenate. The arsenic in the receiver showed no trace of cadmium. The cadmium in the boat was transformed into the white bromide, and was free from arsenic. It was weighed as cadmium bromide. The arsenic was determined as magnesium pyroarsenate.

Experiment.	Cd <sub>3</sub> As <sub>2</sub> O <sub>7</sub> + 2H <sub>2</sub> O taken. Gram.	CdBr <sub>2</sub> obtained. Gram.	CdBr <sub>2</sub> required. Gram.	Difference. Gram.
1.....	0.1041	0.1294	0.1306	0.0012
2.....	0.1104	0.1378	0.1385	0.0007
3.....	0.1168	0.1471	0.1472	0.0001

Experiment.	Cd <sub>3</sub> As <sub>2</sub> O <sub>7</sub> + 2H <sub>2</sub> O taken. Gram.	Mg <sub>3</sub> As <sub>2</sub> O <sub>7</sub> obtained. Gram.	Mg <sub>3</sub> As <sub>2</sub> O <sub>7</sub> required. Gram.	Difference. Gram.
1.....	0.1041	0.0485	0.0494	0.0009

## PREPARATION OF COBALT ARSENATE.

A solution of pure cobalt nitrate was precipitated by a solution of pure sodium pyroarsenate. The purplish-pink salt having the formula  $\text{Co}_3\text{As}_2\text{O}_7 + 2\text{H}_2\text{O}$  was precipitated. It was

<sup>1</sup> *Loc. cit.*

thoroughly washed by decantation, and then gently ignited, until its weight was constant; the blue, anhydrous salt resulted.

#### SEPARATION OF ARSENIC FROM COBALT.

The hydrobromic acid gas attacks the cobalt arsenate in the cold, but the reaction takes place sooner if a low heat is applied. The blue arsenate is changed first to a pink bromide; this, on the application of heat changed to a dark green, anhydrous bromide. The low heat of  $130^{\circ}$  volatilized all the arsenic, leaving all of the cobalt in the boat. The arsenic was estimated in the usual manner.

The boat with its contents, after being cooled in a current of hydrobromic acid gas, and then standing in a desiccator for fifteen minutes, was weighed. Notwithstanding that it absorbs water rapidly, the weight was low if it was calculated as cobalt bromide.

In the first experiment the material taken was 0.1384 gram, the compound weighed 0.1640 gram. If the cobalt compound were cobalt bromide, it should weigh 0.2002 gram. The weight of the compound obtained, 0.1640 gram, is eighty-nine per cent. of the weight required.

In the second experiment, the cobalt arsenate taken was 0.1382 gram; the compound obtained weighed 0.1630 gram. If the cobalt compound were cobalt bromide it should have weighed 0.1999 gram. The weight of the compound obtained, 0.1630 gram, is only 81.5 per cent. of the required weight.

These results led to the conclusion that an oxybromide of indefinite composition is formed.

The next step was to heat the cobalt bromide in a stream of hydrogen, obtaining the metal.

The following satisfactory results were obtained:

Experiment.	$\text{Co}_3\text{As}_2\text{O}_8$ taken. Gram.	Co obtained. Gram.	Co required. Gram.	Difference. Gram.
1.....	0.1382	0.0525	0.0531	0.0006
2.....	0.1244	0.0475	0.0478	0.0003
3.....	0.1228	0.0473	0.0472	0.0001
Experiment.	$\text{Co}_3\text{As}_2\text{O}_8$ taken. Gram.	$\text{Mg}_3\text{As}_2\text{O}_7$ obtained. Gram.	$\text{Mg}_3\text{As}_2\text{O}_7$ required. Gram.	Difference. Gram.
1.....	0.1384	0.0943	0.0949	0.0006
2.....	0.1382	0.0945	0.0947	0.0002

## PREPARATION OF IRON ARSENATE.

Chemically pure ferrous ammonium sulphate was dissolved in water and oxidized with nitric acid, and the ferric salt was crystallized from the solution. The best crystals were dissolved in water and precipitated by a solution of pure sodium pyroarsenate. The yellowish precipitate was washed by decantation, filtered, and the washing continued until the filtrate gave no precipitate with potassium ferrocyanide. The salt was then dried and gently ignited. It is necessary that this ignition should be carefully carried out, as there is danger of decomposing the salt.

## SEPARATION OF ARSENIC FROM IRON.

The results were unsatisfactory. The acid gas acted very energetically on the arsenate. Even in the cold the bromide formed creeps over the sides of the boat, its contents becoming a reddish brown liquid. Unless the current of gas is very slow, and the heat applied very gently, the contents will spatter. The final product was a beautiful red compound, which took up water rapidly. It was dissolved in hydrochloric acid, oxidized with nitric acid, and the iron precipitated with ammonia. Several experiments were carried out; in every case the iron content was low. I was unable to account for this loss, as there was no iron present with the volatile arsenic in the receiver. The residue in the boat was free from arsenic.

## BEHAVIOR OF MINERALS IN HYDROBROMIC ACID GAS.

*Galenite*.—A weighed amount of the mineral was placed in the boat and exposed to the action of the hydrobromic acid gas for two hours. For one hour of the time a temperature of  $100^{\circ}$  was maintained. Before the heat was applied hydrogen sulphide was evolved. After heating, the antimony in the galenite was volatilized and carried over into the receiver, where it was precipitated by the hydrogen sulphide that had been collected in the water, as the orange-colored sulphide of antimony. Tests were applied to the residue in the boat, and it was found to be free from antimony. The volatile products showed no lead, indicating a method for the decomposition and estimation of mineral sulphides that may prove more satisfactory than the present, often tedious, processes.

Smith and Hibbs' previous to this have shown that mimetite loses its arsenic quantitatively when heated in a stream of hydrochloric acid gas. Moyer found in his investigation that niccolite, exposed to the action of hydrochloric acid gas, was only slightly affected. If the niccolite was first dissolved in nitric acid and after evaporation to dryness, exposed to the gas, it was completely decomposed, giving a quantitative separation of the arsenic from the nickel.

#### SUMMARY.

A comparison of the results obtained in separating metals by means of hydrobromic acid gas, and those resulting through the action of hydrochloric acid gas, leads to the conclusion that those metals thus far studied that are volatile in one gas are volatile in the other, and that the same separations may be effected. The principal difference lies in the length of time which is required to make a separation.

The chlorides of antimony and bismuth require from six to eight hours for their complete volatilization. Antimony bromide can be entirely driven out in one hour and a half. The bismuth requires about an hour longer. In the case of arsenic, both the chloride and the bromide are volatilized in an hour and a half.

Some of those metals which do not form volatile compounds with the respective gases, have a tendency in the case of hydrobromic acid, to form oxybromides; the lead compound approximating the formula  $\text{PbO} \cdot 5\text{PbBr}_2$ , while the lead chloride can be weighed directly as  $\text{PbCl}_2$ . Cobalt also forms an oxybromide, while the chloride compound is probably free from oxygen.

After the reaction is finished between the hydrobromic acid gas and copper, cuprous bromide is the result; in the case of hydrochloric acid gas it remains as the cupric compound.

Silver is changed to the chloride and bromide by the action of the respective gases. Cadmium is also changed to a non-volatile chloride and bromide.

Unsatisfactory results were obtained by the use of both reagents in an attempt to separate arsenic from iron.

<sup>1</sup> *Loc. cit.*

## II. INDIUM IN TUNGSTEN MINERALS.

It was about the year 1866 that Hoppe-Seyler,<sup>1</sup> while engaged in the analysis of wolframite from Zinnwald, discovered that indium was present in it.

He obtained 0.028 gram of indium from 122.6 grams of the mineral. He believed that as the latter contained zinc, the indium was probably present in the zinc blende, inasmuch as the quantity of indium found by him was not very much greater than that contained in Freiberg zinc blende. Thinking that indium might possibly be a constant, regular constituent of tungsten-bearing minerals, I resolved to examine some of the latter for this interesting ingredient. The results are appended.

## WOLFRAMITE FROM ZINNWALD.

Three hundred grams of wolframite from Zinnwald were ground and then treated with aqua regia. Several days were required for the complete decomposition of the mineral. The acid solution was then evaporated to dryness, and the residue moistened with dilute hydrochloric acid and taken up with water. The acid was neutralized with sodium carbonate; sodium acetate and a few drops of acetic acid were added. Hydrogen sulphide was then passed through this solution until it was thoroughly saturated with the gas. A yellowish brown precipitate at first came down, soon followed by a black precipitate. These were filtered, redissolved in hydrochloric acid, and the treatment outlined above repeated. It was found necessary to repeat several times before a pure yellow precipitate was obtained.

This yellow compound was dissolved in hydrochloric acid and when examined with the spectroscope gave the bright blue line of indium. The hydrochloric acid solution, upon treatment with ammonium hydroxide, precipitated a white gelatinous mass. This was filtered, dried, and ignited, when a yellow residue remained, which was the oxide of indium. Its weight was 0.0145 gram.

The filtrate from the indium hydroxide was evaporated to a small bulk, and treated with ammonium hydroxide. The solution was bright blue, and on treatment with ammonium sulphide

<sup>1</sup> *Ann. Chem.* (Liebig), 140, 247.

gave a grayish, chocolate-colored precipitate. This all dissolved in dilute hydrochloric acid, with the exception of a black sediment. A copper bead was obtained with this insoluble portion.

Hydrogen sulphide when passed through the filtrate gave no precipitate, but after neutralizing with ammonium hydroxide and adding ammonium sulphide, a dirty white precipitate came down. This gave Rinman's green, an evidence of zinc.

#### WOLFRAMITE FROM CORNWALL, ENGLAND.

The mineral was an impure specimen. After it was broken into small pieces, the purest portions were ground up, and 300 grams were treated with aqua regia. The solution was poured off, the mineral again treated with acid, and the solution added to the first one. This treatment was continued until all of the mineral was decomposed.

The aqua regia solution was evaporated to dryness, taken up with hydrochloric acid and water, and after neutralization with sodium carbonate and addition of sodium acetate and acetic acid, was treated with hydrogen sulphide gas. The precipitate obtained was reddish brown in color. It dissolved in hydrochloric acid. When examined with the spectroscope, indium could not be discovered.

The hydrochloric acid solution was then examined as under the Zinnwald wolframite, but no zinc could be detected.

#### HÜBNERITE FROM COLORADO.

One hundred and fifty grams of hübnerite from Colorado were treated with aqua regia, and the further treatment for the isolation of indium, as already outlined, was carried out. Hydrogen sulphide caused a reddish precipitate, which dissolved in hydrochloric acid, and proved not to be indium. Zinc was also absent.

#### SCHREELITE FROM NEW ZEALAND.

Two hundred and fifty grams of this mineral were decomposed with aqua regia. There resulted the usual reddish precipitate with hydrogen sulphide in the acetate solution.

The hydrochloric acid solution when tested with the spectroscope gave a blue line, which at first was thought to be the



indium line; but on closer examination it proved to be the strontium line. The indium and strontium lines lie close together. The line which I found had a wave-length of  $4.61 \times 10^{-5}$ , corresponding to the line  $\text{Sr}\rho$ ; whereas the indium lines are  $\text{In}_\alpha 4.51 \times 10^{-5}$  and  $\text{In}_\beta 4.10 \times 10^{-5}$ .

The acid solution, neutralized with sodium carbonate, gave a white precipitate; on drying, a yellow powder was obtained, which proved to be calcium carbonate. Zinc was not present.

#### SCHEELITE FROM BOHEMIA.

A pure specimen of this mineral was subjected to the same treatment as has been described. The same results were obtained. No indium could be detected and the absence of zinc was proved.

The care exercised in the selection of material, and the large quantities employed, while working with every precaution, would seem to justify the conclusion that indium cannot be regarded as an associate of tungsten in its natural derivatives; that most probably the suspicion of Hoppe-Seyler in regard to its origin, *vis.*, blende, is correct, for it was only in the Zinnwald specimen that I could detect it.

UNIVERSITY OF PENNSYLVANIA.

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#### NEW BOOKS.

**EXPLOSIVE MATERIALS.** The Phenomena and Theories of Explosion and the Classification, Constitution, and Preparation of Explosives. BY 1ST LIEUT. JOHN P. WISSER, 1st Art., U. S. A. New York: D. Van Nostrand Company. 1898. Price, 50 cents.

This little book, which is issued as No. 70 in Van Nostrand's Science Series, bears the same leading title as the No. 70 of this series issued in 1883, but, while the contents of the 1883 edition consisted of a translation of "Berthelot's Lecture on Explosive Materials" by Dr. Marcus Benjamin, a translation of "Braun's Historical Sketch of Gunpowder" by Lieut. John P. Wisser, and a "Bibliography of Works on Explosives" by W. H. Farrington, the present edition contains an original essay by Lieut. Wisser only, which is based upon the lecture of Berthelot, but, which includes the more recently adopted theories, and much descriptive matter. Where considerable space is given to the display of graphic formulas of substances used in the manu-

facture of explosive materials, it is obviously impossible to give any lengthy descriptions of processes of manufacture in 145 small pages of a pocket volume, such as this is, yet the author has contrived to put a very large amount of reliable information between its covers, and his descriptions, though brief, are clear and accurate. It is greatly to be regretted that the publishers have not done their part as well as the author has done his, and that the volume should be marred by typographical errors while its general make-up is quite unattractive. Nevertheless the book may be recommended as a useful one to keep at hand as a ready reference work on this important subject.

CHARLES E. MUNROE.

### BOOKS RECEIVED.

Commercial Organic Analysis. By Alfred H. Allen. Vol. I. Introduction, Alcohols, Neutral Alcoholic Derivatives, Sugars, Starch, and its Isomers, Vegetable Acids, etc. Philadelphia: P. Blakiston's Son & Co. 1898. xii + 557 pp. Price \$4.50.

A Text-book of Elementary Analytical Chemistry, Qualitative and Volumetric. By John H. Long, M.S., Sc.D. Chicago: E. H. Colegrove. 1898. viii + 278 pp. Price \$1.50.

The Discharge of Electricity through Gases. Lectures delivered on the occasion of the sesquicentennial celebration of Princeton University by J. J. Thomson, Professor of the University of Cambridge. New York: Charles Scribner's Sons. 1898. x + 203 pp. Price \$1.00.

The Characters and Methods of Assay of the Official Hypophosphites and a Note on the Mydiatic Alkaloids. By H. A. D. Jowett, D. Sc. The Wellcome Research Laboratories, Snow Hill, London, E. C., England. 20 pp.

Cultivation of Tobacco in Sumatra. By Emile Mulder. U. S. Department of Agriculture, Washington, D. C. 39 pp.

Report on an Investigation of Analytical Methods for Distinguishing between the Nitrogen of Proteids and that of the Simpler Amids or Amido-Acids. By J. W. Mallet. With a chapter on the Separation of Flesh Bases from Proteid Matters by Means of Bromine. By H. W. Wiley. Bulletin No. 54. U. S. Department of Agriculture, Division of Chemistry, Washington, D. C. 1898. 30 pp.

Ores of Nova Scotia. Gold, Lead, and Copper. By E. Gilpin, Jr., M.A., LL.D., F.R.S.C., etc. Halifax, N. S.: Commissioner of Public Works and Mines. 1898. 46 pp.

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### I. DERIVATIVES OF THE TETRACHLORIDES OF ZIRCONIUM, THORIUM, AND LEAD.<sup>1</sup>

BY J. MERRITT MATTHEWS.

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#### I. INTRODUCTION.

THE tetrachlorides of several of the members of Group IV have been studied in their deportment with certain organic nitriles and amines, and the results seem to indicate that there is a general tendency toward reactions between these tetrachlorides and the latter-named reagents, giving rise to definitely constituted compounds. That is to say, the tetrachlorides of Group IV appear to possess an acidic character in their ability to combine with certain organic bases to form neutral salts. This behavior has already been studied with reference to the tetrachlorides of carbon, silicon, titanium, and tin; and although the data at our command are neither as connected nor as complete as might be desired, nevertheless, they may be regarded as sufficient to establish a characteristic group reaction. In these reactions, however, there appear to be several unaccountable fluctuations and divergences among the different members of the group. It would be natural to expect a difference in the behavior of the metallic subgroup including germanium, tin, and lead, from the more non-metallic subgroup including titanium, zirconium, and thorium. But such a conclusion does not

<sup>1</sup> From author's thesis for the Degree of Doctor of Philosophy.

appear to receive the necessary strength from the actual facts observed in order to give it a sure foundation; for titanium seems to exhibit a greater analogy in its reactions to those of tin than to any other. The number of reactions studied, however, have been so few that it would be presumptuous to formulate a comprehensive law regarding the general reactions of the two subgroups in question, and in consequence of there being no such law established, it would be illogical to argue that apparently diverging reactions pointed necessarily to inconsistencies in the behavior of the two subgroups.

The tetrachlorides of silicon, titanium, and tin have been rather comprehensively studied in their behavior toward nitriles and amines. Titanium tetrachloride has been found to be reactive with formonitrile, acetonitrile, benzonitrile, toluonitrile, succinonitrile, chlorcyanogen, sulphur monochloride, phosphorus pentachloride, and the vapors of aqua regia. The tetrachloride of tin also exhibits analogous reactions with every one of the above-mentioned reagents; silicon tetrachloride, however, shows no evidence of reacting with these compounds.

All three of these tetrachlorides give derivatives with ammonia and aromatic amines, as does also carbon tetrachloride. With the fatty amines, however, only the chlorides of silicon and tin have been found to be reactive.

## 2. PREPARATION OF THE TETRACHLORIDES OF ZIRCONIUM, THORIUM, AND LEAD.

### A. ZIRCONIUM TETRACHLORIDE.

The zirconium tetrachloride used in this research was prepared in the following manner: Carefully selected crystals of zircon were finely powdered and fused with acid potassium sulphate; the fusion was lixiviated with water, and filtered; the residue was dried and fused with potassium hydroxide in a nickel dish. This fusion, after being digested with water, and filtered, left a white amorphous residue of zirconium dioxide. The oxide was mixed with pulverized starch and molasses to a thick batter, which was then rolled into small pellets about one centimeter in diameter. These were slowly dried in an air oven until all moisture was expelled, when they were transferred to a covered silver crucible and charred until no more vapors were

evolved. These pellets, containing zirconium dioxide intimately mixed with pure charcoal, were placed in a long glass combustion tube, and strongly heated in a current of dry chlorine gas. Zirconium tetrachloride was formed by this procedure, and collected in the cooler part of the tube in the form of a white powder or minute crystals. The salt thus obtained was dissolved in ether which had been carefully dehydrated by repeated distillation over sodium, until thin slices of the metal remained untarnished on being in contact with the ether for several days. The zirconium tetrachloride in the form of this ethereal solution was used in all the experiments, as it gave a convenient and uniform method for testing the reactions.

#### B. THORIUM TETRACHLORIDE.

This salt was prepared in a manner precisely analogous to that given for zirconium. The dioxide,  $\text{ThO}_2$ , was obtained from a quantity of the nitrate which was available for the purpose, by precipitation with ammonium hydroxide and subsequent ignition. The tetrachloride was dissolved in dehydrated ether, as in the case of the zirconium salt, and this solution was used in all of the reactions.

#### C. LEAD TETRACHLORIDE.

This compound was prepared by the method of Friedrich.<sup>1</sup> One part of lead chloride was suspended in twenty parts of concentrated hydrochloric acid, and a current of chlorine gas was conducted through the liquid until nearly all of the lead dichloride had gone into solution, which required about twenty hours. The temperature of the liquid during the entire process was kept at about  $4^\circ \text{C}$ . by means of a freezing-mixture. The yellow-colored liquid which resulted from this treatment consisted of a solution of lead tetrachloride in concentrated hydrochloric acid. Two parts of ammonium chloride dissolved in ten parts of water were then added, and a bright lemon-yellow crystalline precipitate was produced, consisting of the ammonium double salt of lead tetrachloride, which, according to Friedrich, has the formula  $\text{PbCl}_4 \cdot 2\text{NH}_4\text{Cl}$ . Classen and Zahorski,<sup>2</sup> however, apparently obtain the same salt—by practically the same

<sup>1</sup> *Ber. d. chem. Ges.*, 26, 1434.

<sup>2</sup> *Ztschr. anal. Chem.*, 4, 100.

method—and they ascribe to it the formula  $2\text{PbCl}_2 \cdot 5\text{NH}_4\text{Cl}$ . The ammonium double salt was filtered off and washed free from hydrochloric acid and chlorine with absolute alcohol and ether. A portion of this salt was placed in a separatory funnel and digested with fuming sulphuric acid of specific gravity 1.879. A brisk reaction took place and yellow oily drops of lead tetrachloride soon separated out; these were washed by decantation several times with fuming sulphuric acid, and finally dissolved in chloroform which had been carefully dehydrated over fuming sulphuric acid. This chloroform solution of the lead tetrachloride was used for all the reactions; but fresh portions and solutions had to be made for each experiment, as the tetrachloride decomposed into the lower chloride in a few hours. It was found impossible to work with the liquid tetrachloride itself, as it was immediately decomposed on coming in contact with the air, and even decomposed in about twelve hours when kept under fuming sulphuric acid. The strength of the acid used for the decomposition of the ammonium double salt is an important factor in this preparation, as an acid of less strength than that used above will fail to give the lead tetrachloride in any appreciable quantity.

### 3. THE ACTION OF NITRILES, ETC., ON THE TETRACHLORIDES.

As zirconium occupies the next position to titanium in the same subgroup, it was natural to suppose that its tetrachloride would exhibit reactions with the nitriles somewhat analogous to those of the latter element, and that the analogy might also be followed into the fatty and aromatic amines. Contemporary with this present work there was carried to completion in this same laboratory a study of the reactions of silicon tetrachloride; and as both tin and titanium have been studied in this same connection, it was considered that a research into the possible derivatives of the allied members of this group might lead to results which would be useful in establishing analogies and comparisons between the different members of 'Group IV, as viewed from their respective behavior with the reagents used in this study. By this means it was thought probable that a definite law might be formulated for the group with regard to these

reactions, and that the heterogeneous data, heretofore lying dissociated and useless, might be brought together and systematically understood.

*a. Vapors of Aqua Regia.*—The dry vapors of aqua regia conducted into the solution of zirconium tetrachloride gave no reaction, the solution only becoming discolored by the gases, which were again liberated on raising the temperature. Portions of the dry zirconium salt were also placed in a porcelain boat, and heated in a current of the dry vapors of aqua regia; but the salt appeared to volatilize unchanged, and no compound was formed. In this behavior zirconium shows a deviation from that of titanium, as the tetrachloride of the latter reacts readily with the vapors of aqua regia, giving a compound corresponding to the formula  $3\text{TiCl}_4 \cdot 2\text{NO}_2\text{Cl}$ , Hampe.<sup>1</sup> An analogous compound with tin tetrachloride has been prepared by the same investigator. Baeyer<sup>2</sup> also records the compound  $\text{SnCl}_4 \cdot 2\text{NOCl}$ .

The solutions of the tetrachlorides of thorium and lead behaved similarly to that of zirconium, and gave no derivatives.

*b. Nitrogen Dioxide.*—This gas, obtained by heating lead nitrate, on being conducted into the solutions of the tetrachlorides, gave no reaction beyond a simple solution of the gas. The dry salts of zirconium and thorium, heated in a current of the gas, volatilized unchanged and gave no compound.

*c. Sulphur Monochloride.*—On mixing this substance with the solutions of the tetrachlorides, no reaction was observed.

*d. Chlorides of Phosphorus.*—The action of both the tri- and pentachlorides of phosphorus was tried on the solutions of the tetrachlorides, but no combination resulted.

*e. Dicyanogen.*—On conducting this gas into the solutions of the tetrachlorides, no reaction took place; nor does it seem to have formed any compounds with the corresponding salts of titanium or tin.

*f. Formonitrile.*—Though both titanium and tin tetrachlorides give derivatives with hydrocyanic acid, yet no product was obtained by allowing this compound to act on the three tetrachlorides here investigated.

*g. Cyanogen Chloride.*—It was prepared by the action of chlo-

<sup>1</sup> *Ann. Chem.* (Liebig), 126, 43.

<sup>2</sup> *Ber. d. chem. Ges.*, 7, 1639.

rine on mercuric cyanide, but it gave no reactions with the solutions of the tetrachlorides.

*h. Acetonitrile.*—The vapors of this nitrile passed into the solutions of the tetrachlorides yielded no compounds, although derivatives have been obtained with the titanium and tin salts.

*i. Bensonitrile.*—Like acetonitrile, this aromatic body yielded no derivatives with the tetrachlorides.

#### SUMMARY.

From these experiments it is to be observed that the nitriles and the other reagents here used, which for the most part gave additive compounds with the tetrachlorides of titanium and tin, are without action on the corresponding salts of zirconium, thorium, and lead.

#### 4. ACTION OF FATTY AND AROMATIC AMINES.

It was in this field that positive results were at last encountered. Silicon, titanium, and tin tetrachlorides all give compounds with the amines, and analogy would lead us to expect that the chlorides here used would behave in a similar manner, as indeed was the case. These derivatives with the amine bases, including ammonia, are apparently peculiar additive products, showing that these tetrachlorides, in common with the other chlorides of this group, possess an acid character.

The compounds herein described were obtained by the simple addition of the pure anhydrous reagents to the solutions of the respective tetrachlorides. The zirconium and thorium derivatives, for the most part, were white flocculent precipitates; the lead salts, however, gave compounds of various colors.

The analysis of these derivatives was carried out in the following manner: With the zirconium and thorium compound a weighed quantity was placed in a small beaker-glass and covered with nitric acid containing a solution of silver nitrate, and gently warmed. This sufficed to decompose the substance, the chlorine present being precipitated as silver chloride. The liquid was diluted with water, the chloride filtered off, and from its weight the chlorine was estimated. Excess of ammonia water was added to the filtrate, and the resulting precipitate of zirconium or thorium hydroxide was filtered off and ignited to the corre-



sponding dioxide, from the weight of which the zirconium or thorium was estimated. The nitrogen present in the ammonia derivatives was determined by heating a portion with a strong solution of sodium hydroxide, and passing the evolved ammonia into a standardized solution of hydrochloric acid, and either titrating the excess of acid with standard alkali, or precipitating the ammonia in the usual manner with a solution of platinic chloride, and from the weight of the platinum left after ignition calculating the quantity of nitrogen. With the amine derivatives the Kjeldahl method was employed; and the Will and Varrentrap method was used for the quinoline and pyridine compounds. The lead compounds were decomposed with warm nitric acid, and the lead determined as sulphate by evaporation with sulphuric acid in the usual manner, the chlorine being determined by heating the compound with sulphuric acid in a distilling flask, passing the evolved hydrochloric acid gas into a solution of silver nitrate, and weighing the silver chloride as usual. The nitrogen present was estimated as with the zirconium and thorium derivatives.

#### A. AMMONIA.

Paykull<sup>1</sup> obtained a compound of zirconium tetrachloride with ammonia by heating the former with  $\text{NH}_4\text{Cl}$ , and to this compound he ascribes the formula  $\text{ZrCl}_4 \cdot 4\text{NH}_3$ . Besson<sup>2</sup> has also obtained an ammonia derivative with silicon tetrachloride, giving it the formula  $\text{SiCl}_4 \cdot 6\text{NH}_3$ . With tin tetrachloride Rose<sup>3</sup> obtained the compound  $\text{SnCl}_4 \cdot 4\text{NH}_3$ , though Persoz<sup>4</sup> claims to have made  $\text{SnCl}_4 \cdot 6\text{NH}_3$ . With titanium tetrachloride Rose<sup>3</sup> obtained the compound  $\text{TiCl}_4 \cdot 4\text{NH}_3$ , though Persoz<sup>5</sup> gives the formula as  $\text{TiCl}_4 \cdot 6\text{NH}_3$ .

*a. Zirconium Tetrachloride,  $\text{ZrCl}_4 \cdot 8\text{NH}_3$ .* — On passing dry ammonia gas into the solution of zirconium tetrachloride, a white flocculent precipitate was immediately produced, with considerable evolution of heat. This compound on drying appeared to be stable in the air, though on gently heating it

<sup>1</sup> *Ber. d. chem. Ges.*, 6, 1467.

<sup>2</sup> *Compt. rend.*, 110, 240.

<sup>3</sup> *Pogg. Ann.*, 20, 147.

<sup>4</sup> *Ann. chim. phys.*, 46, 305.

<sup>5</sup> *Vide supra*.

gave off fumes of ammonium chloride. Its analysis showed the presence of eight molecules of ammonia.

I. 0.5625 gram material gave :

0.8729 gram silver chloride = 0.2161 gram chlorine = 38.42 per cent. chlorine.

0.1860 gram zirconium dioxide = 0.1374 gram zirconium = 24.44 per cent. zirconium.

II. 0.1862 gram material gave :

0.2881 gram silver chloride = 0.0713 gram chlorine = 38.30 per cent. chlorine.

0.0623 gram zirconium dioxide = 0.0460 gram zirconium = 24.71 per cent. zirconium.

0.0624 gram material gave 0.0228 gram ammonia = 36.60 per cent. ammonia.

0.5625 gram material gave 0.2084 gram ammonia = 37.05 per cent. ammonia.

	Calculated for $\text{ZrCl}_4 \cdot 8\text{NH}_3$ .	I.	Found. II.
Chlorine .....	38.52	38.42	38.30
Zirconium .....	23.58	24.44	24.71
Ammonia .....	36.90	36.60	37.05

$\text{ZrCl}_4 \cdot 2\text{NH}_3$ .—On passing dry ammonia gas over the solid zirconium tetrachloride contained in a porcelain boat, a considerable evolution of heat was observed, evidently showing that combination resulted. The compound thus obtained was white in color, fumed in the air, and rapidly took up moisture, rendering it difficult to analyze with accuracy.

0.5304 gram zirconium tetrachloride, after being treated with ammonia gas for two hours, on reweighing gave 0.6247 gram.

This on analysis gave :

1.3778 gram silver chloride = 0.3163 gram chlorine = 50.67 per cent. chlorine.

0.2927 gram zirconium dioxide = 0.2163 gram zirconium = 34.62 per cent. zirconium.

	Calculated for $\text{ZrCl}_4 \cdot 2\text{NH}_3$ .	Found.
Chlorine .....	51.81	50.67
Zirconium .....	33.21	34.26
	Gram.	Gram.
Increase in weight.....	0.0917	0.0943

$\text{ZrCl}_4 \cdot 4\text{NH}_3$ .—On heating zirconium tetrachloride in a current of dry ammonia gas, a compound was obtained which was white in color, and unstable on exposure to the air.

0.4713 gram zirconium tetrachloride being gently heated (to about  $100^\circ \text{C.}$ ) in ammonia gas, on reweighing gave 0.6123 gram.

This on analysis gave :

1.1397 gram silver chloride = 0.2821 gram chlorine = 46.07 per cent. chlorine.

0.2588 gram zirconium dioxide = 0.1912 gram zirconium = 31.23 per cent. zirconium.

	Calculated for $\text{ZrCl}_4 \cdot 4\text{NH}_3$ .	Found.
Chlorine.....	47.24	46.07
Zirconium.....	30.14	31.23
	Gram.	Gram.
Increase in weight.....	0.1378	0.1410

These results seem to indicate that zirconium tetrachloride may be combined with ammonia in three proportions, depending upon the conditions under which the combination is brought about. When in ethereal solution it takes up eight molecules of ammonia, giving  $\text{ZrCl}_4 \cdot 8\text{NH}_3$ ; the dry salt unaided by heat gives  $\text{ZrCl}_4 \cdot 2\text{NH}_3$ ; and with the aid of heat the latter also gives the compound  $\text{ZrCl}_4 \cdot 4\text{NH}_3$ . All of these bodies are white in color, the first one only being stable in the air. The last of the above derivatives seems to be identical with the one obtained by Paykull.

*b. Thorium Tetrachloride.*—As the field of thorium derivatives has not been investigated in any very exhaustive manner, one would not be likely to encounter any preceding research in the rather remote class of compounds herein dealt with. Chydenius,<sup>1</sup> however, has prepared a derivative of thorium tetrachloride with ammonium chloride, to which he has given the formula  $\text{ThCl}_4 \cdot 8\text{NH}_4\text{Cl}$ . It is of interest to note that the compound prepared in this present research also contains the same molecular proportions of ammonia to thorium.

$\text{ThCl}_4 \cdot 8\text{NH}_3$ .—Dry ammonia gas passed into the solution of thorium tetrachloride produced a white flocculent precipitate, which, on drying, continued stable in the air. On heating, it

<sup>1</sup> *Jsb. Chem.*, 1863, 194.

decomposed with the evolution of fumes of ammonium chloride.

I. 0.5870 gram material gave :

0.6526 gram silver chloride = 0.1616 gram chlorine = 27.52 per cent. chlorine.

0.3054 gram thorium dioxide = 0.2684 gram thorium = 45.73 per cent. thorium.

II. 0.6212 gram material gave :

0.5928 gram silver chloride = 0.1715 gram chlorine = 27.61 per cent. chlorine.

0.3212 gram thorium dioxide = 0.2824 gram thorium = 45.46 per cent. thorium.

0.5172 gram material gave 0.1366 gram ammonia = 26.41 per cent. ammonia.

	Calculated for $\text{ThCl}_4 \cdot 8\text{NH}_3$ .	I.	Found. II.
Chlorine .....	27.80	27.52	27.61
Thorium.....	45.55	45.73	45.46
Ammonia.....	26.64	26.41	....

$\text{ThCl}_4 \cdot 6\text{NH}_3$ .—On allowing dry ammonia gas to pass over a portion of thorium tetrachloride placed in a porcelain boat, a considerable evolution of heat was observed, the ammonia evidently reacting with the salt. The resulting compound was white in color, and fumed in moist air, though it appeared to be more stable than the corresponding zirconium derivative obtained under the same conditions.

0.4217 gram material, on being treated with ammonia gas for two hours, on reweighing gave 0.5352 gram. This on analysis gave :

0.6274 gram silver chloride = 0.1553 gram chlorine = 29.01 per cent. chlorine.

0.3021 gram thorium dioxide = 0.2656 gram thorium = 49.62 per cent. thorium.

	Calculated for $\text{ThCl}_4 \cdot 6\text{NH}_3$ .	Found.
Chlorine .....	29.79	29.01
Thorium .....	48.80	49.62
Gram.		Gram.
Increase in weight.....	0.1148	0.1135

On gently heating thorium tetrachloride to about 100° C. in a current of ammonia gas, a compound was obtained identical

with the one just described above; it possessed the same appearance and analyzed for the same formula. At a higher temperature decomposition seemed to take place and copious fumes of ammonium chloride were formed.

*c. Lead Tetrachloride,  $\text{PbCl}_4 \cdot 4\text{NH}_3$ .*—On treating the chloroform solution of lead tetrachloride with dry ammonia gas, an orange-yellow precipitate was at first produced, which rapidly became white in color as more ammonia was absorbed. A great amount of heat was evolved in the reaction, and the compound continued stable in the air.

I. 0.3600 gram material gave :

0.2597 gram lead sulphate = 0.1774 gram lead = 49.30 per cent. lead.

0.2614 gram material gave :

0.3205 gram silver chloride = 0.0816 gram chlorine = 33.76 per cent. chlorine.

II. 0.2582 gram material gave :

0.1874 gram lead sulphate = 0.1281 gram lead = 49.62 per cent. lead.

0.2075 gram material gave :

0.2844 gram silver chloride = 0.0704 gram chlorine = 33.92 per cent. chlorine.

0.4201 gram material gave :

0.3817 gram platinum = 0.0664 gram ammonia = 15.81 per cent. ammonia.

	Calculated for $\text{PbCl}_4 \cdot 4\text{NH}_3$ .	I.	Found. II.
Lead.....	49.88	49.30	49.62
Chlorine.....	34.05	33.76	33.92
Ammonia.....	16.07	15.81	....

$\text{PbCl}_4 \cdot 2\text{NH}_3$ .—By using a more concentrated solution of lead tetrachloride, and interrupting the treatment with ammonia gas before all of the lead salt was neutralized, an orange-yellow precipitate was obtained. This fumed in the air and decomposed on standing. Its analysis indicated the above formula.

0.3017 gram material gave :

0.2375 gram lead sulphate = 0.1622 gram lead = 53.75 per cent. lead.

0.2332 gram material gave :

0.3525 gram silver chloride = 0.0873 gram chlorine = 37.42 per cent. chlorine.

0.2716 gram material gave :

0.1430 gram platinum = 0.0249 gram ammonia = 9.16 per cent. ammonia.

	Calculated for $\text{PbCl}_4 \cdot 2\text{NH}_3$ .	Found.
Lead .....	54.16	53.75
Chlorine.....	37.00	37.42
Ammonia.....	8.85	9.16

#### B. METHYLAMINE.

*a. Zirconium Tetrachloride,  $\text{ZrCl}_4 \cdot 4\text{CH}_3\text{NH}_2$ .*—On conducting the vapors of methylamine into the solution of zirconium tetrachloride, a white flocculent precipitate was formed. Analysis showed that it followed the same general type as the other derivatives.

I. 0.2417 gram material gave :

0.3833 gram silver chloride = 0.0949 gram chlorine = 39.26 per cent. chlorine.

0.0838 gram zirconium dioxide = 0.0619 gram zirconium = 25.62 per cent. zirconium.

II. 0.5432 gram material gave :

0.8674 gram silver chloride = 0.2147 gram chlorine = 39.53 per cent. chlorine.

0.1786 gram zirconium dioxide = 0.1339 gram zirconium = 25.65 per cent. zirconium.

0.6021 gram material gave :

0.1165 gram ammonia = 0.0969 gram nitrogen = 15.95 per cent. nitrogen.

	Calculated for $\text{ZrCl}_4 \cdot 4\text{CH}_3\text{NH}_2$ .	Found.	
		I.	II.
Chlorine.....	39.82	39.36	39.53
Zirconium .....	25.41	25.62	25.65
Nitrogen.....	16.18	15.95	....

*b. Thorium Tetrachloride,  $\text{ThCl}_4 \cdot 4\text{CH}_3\text{NH}_2$ .*—The compound obtained with thorium tetrachloride showed the presence of four molecules of the base. Indeed this seems to be the general type after which all these derivatives are modeled.

0.6513 gram material gave :

0.7451 gram silver chloride = 0.1802 gram chlorine = 28.32 per cent. chlorine.

0.3461 gram thorium dioxide = 0.3040 gram thorium = 46.71 per cent. thorium.

0.5318 gram material gave :

0.0712 gram ammonia = 0.0587 gram nitrogen = 11.03 per cent. nitrogen.

	Calculated for $\text{ThCl}_{4.4}\text{CH}_3\text{NH}_2$ .	Found.
Chlorine.....	28.48	28.32
Thorium.....	46.65	46.71
Nitrogen .....	11.24	11.03

*c. Lead Tetrachloride,  $\text{PbCl}_{4.4}\text{CH}_3\text{NH}_2$ .*—The compound obtained with lead tetrachloride was also white in color, and stable in the air. Analysis proved it to be analogous to the preceding derivatives.

0.2506 gram material gave :

0.2969 gram silver chloride = 0.0735 gram chlorine = 29.32 per cent. chlorine.

0.2716 gram material gave :

0.1757 gram lead sulphate = 0.1200 gram lead = 44.17 per cent. lead.

0.2517 gram material gave :

0.2005 gram platinum = 0.0289 gram nitrogen = 11.42 per cent. nitrogen.

	Calculated for $\text{PbCl}_{4.4}\text{CH}_3\text{NH}_2$ .	Found.
Chlorine.....	30.02	29.32
Lead .....	43.76	44.17
Nitrogen .....	11.84	11.42

### C. ETHYLAMINE.

*a. Zirconium Tetrachloride,  $\text{ZrCl}_{4.4}\text{C}_2\text{H}_5\text{NH}_2$ .*—As would be expected from its behavior with the preceding amine, zirconium tetrachloride was found to yield a derivative with ethylamine.

0.5418 gram material gave :

0.7478 gram silver chloride = 0.1856 gram chlorine = 34.26 per cent. chlorine.

0.1619 gram zirconium dioxide = 0.1196 gram zirconium = 22.08 per cent. zirconium.

0.6516 gram material gave :

0.0861 gram ammonia = 0.0709 gram nitrogen = 10.89 per cent. nitrogen.

	Calculated for $\text{ZrCl}_4 \cdot 4\text{C}_2\text{H}_5\text{NH}_2$ .	Found.
Chlorine.....	34.42	34.26
Zirconium.....	21.96	22.08
Nitrogen .....	10.79	10.89

*b. Thorium Tetrachloride,  $\text{ThCl}_4 \cdot 4\text{C}_2\text{H}_5\text{NH}_2$ .*—Ethylamine gave a white compound with thorium tetrachloride.

0.2102 gram material gave :

0.2137 gram silver chloride = 0.0528 gram chlorine = 25.12 per cent. chlorine.

0.0995 gram thorium dioxide = 0.0874 gram thorium = 41.58 per cent. thorium.

0.5912 gram material gave :

0.0712 gram ammonia = 0.0587 gram nitrogen = 9.92 per cent. nitrogen.

	Calculated for $\text{ThCl}_4 \cdot 4\text{C}_2\text{H}_5\text{NH}_2$ .	Found.
Chlorine.....	25.60	25.12
Thorium .....	41.94	41.58
Nitrogen .....	10.10	9.92

*c. Lead Tetrachloride,  $\text{PbCl}_4 \cdot 4\text{C}_2\text{H}_5\text{NH}_2$ .*—Ethylamine gave at first a yellow precipitate with the solution of lead tetrachloride, which went over to a white compound on the addition of more ethylamine.

0.2072 gram material gave :

0.2220 gram silver chloride = 0.0550 gram chlorine = 25.52 per cent. chlorine.

0.2506 gram material gave :

0.1459 gram lead sulphate = 0.0996 gram lead = 39.76 per cent. lead.

0.3817 gram material gave :

0.2746 gram platinum = 0.0394 gram nitrogen = 10.32 per cent. nitrogen.

	Calculated for $\text{PbCl}_4 \cdot 4\text{C}_2\text{H}_5\text{NH}_2$ .	Found.
Chlorine.....	26.84	26.52
Lead .....	39.13	39.76
Nitrogen .....	10.59	10.32



## D. PROPYLAMINE.

*a. Zirconium Tetrachloride*,  $\text{ZrCl}_4 \cdot 4\text{C}_3\text{H}_7\text{NH}_2$ .—With propylamine, zirconium tetrachloride gave a white compound similar in appearance to the foregoing derivatives.

0.3390 gram material gave :

0.4112 gram silver chloride = 0.1020 gram chlorine = 30.10 per cent. chlorine.

0.0897 gram zirconium dioxide = 0.0663 gram zirconium = 19.55 per cent. zirconium.

0.6229 gram material gave :

0.0892 gram ammonia = 0.0736 gram nitrogen = 11.80 per cent. nitrogen.

	Calculated for $\text{ZrCl}_4 \cdot 4\text{C}_3\text{H}_7\text{NH}_2$ .	Found.
Chlorine.....	30.30	30.10
Zirconium.....	19.33	19.55
Nitrogen .....	11.96	11.80

*b. Thorium Tetrachloride*,  $\text{ThCl}_4 \cdot 4\text{C}_3\text{H}_7\text{NH}_2$ . — Propylamine gave a white compound with thorium tetrachloride.

0.2682 gram material gave :

0.2537 gram silver chloride = 0.0628 gram chlorine = 23.40 per cent. chlorine.

0.1167 gram thorium dioxide = 0.1026 gram thorium = 38.22 per cent. thorium.

0.4213 gram material gave :

0.0460 gram ammonia = 0.0379 gram nitrogen = 9.01 per cent. nitrogen.

	Calculated for $\text{ThCl}_4 \cdot 4\text{C}_3\text{H}_7\text{NH}_2$ .	Found.
Chlorine.....	23.25	23.40
Thorium .....	38.09	38.22
Nitrogen .....	9.18	9.01

*c. Lead Tetrachloride*,  $\text{PbCl}_4 \cdot 4\text{C}_3\text{H}_7\text{NH}_2$ .—Propylamine at first gave a dark reddish brown precipitate with lead tetrachloride soon becoming almost white in color, having a faint yellow tinge.

0.2507 gram material gave :

0.2065 gram silver chloride = 0.0511 gram chlorine = 20.39 per cent. chlorine.

0.2672 gram material gave :

0.1195 gram lead sulphate = 0.0817 gram lead = 30.56 per cent. lead.

0.2817 gram material gave :

0.1513 gram platinum = 0.0217 gram nitrogen = 7.82 per cent. nitrogen.

	Calculated for $\text{PbCl}_4 \cdot 4\text{C}_6\text{H}_5\text{NH}_2$ .	Found.
Chlorine.....	20.73	20.39
Lead .....	30.22	30.56
Nitrogen .....	8.28	7.82

#### E. ANILINE.

Schiff<sup>1</sup> has obtained a compound of tin tetrachloride with aniline, to which he has given the formula  $\text{SnCl}_4 \cdot 4\text{C}_6\text{H}_5\text{NH}_2$ , while with titanium tetrachloride Leeds<sup>2</sup> describes a derivative having the formula  $\text{TiCl}_4 \cdot 4\text{C}_6\text{H}_5\text{NH}_2$ .

In all of these derivatives the aniline appears to be merely additive. With silicon tetrachloride, however, aniline seems to form a substitution product corresponding to the formula  $\text{SiCl}_4 \cdot (\text{C}_6\text{H}_5\text{NH}_2)_4$ ; Harden,<sup>3</sup> Reynolds,<sup>4</sup> and Harold.<sup>5</sup>

a. *Zirconium Tetrachloride*,  $\text{ZrCl}_4 \cdot 4\text{C}_6\text{H}_5\text{NH}_2$ .—On the addition of aniline to the solution of zirconium tetrachloride a grayish flocculent precipitate was produced. This was carefully washed with anhydrous ether until all traces of aniline were removed. It appeared to be stable on drying, and its analysis showed the presence of four molecules of aniline.

I. 0.5382 gram material gave :

0.5053 gram silver chloride = 0.1251 gram chlorine = 23.25 per cent. chlorine.

0.1080 gram zirconium dioxide = 0.0798 gram zirconium = 14.83 per cent. zirconium.

II. 0.4817 gram material gave :

0.4538 gram silver chloride = 0.1123 gram chlorine = 23.32 per cent. chlorine.

0.0982 gram zirconium dioxide = 0.0726 gram zirconium = 15.06 per cent. zirconium.

I. 0.5382 gram material gave :

<sup>1</sup> *Jsb. Chem.*, 1863, 412.

<sup>2</sup> *This Journal*, 3, 145.

<sup>3</sup> *J. Chem. Soc.*, 51, 40.

<sup>4</sup> *Ibid.*, 55, 474.

<sup>5</sup> *Thesis*, Univ. of Pennsylvania, 1897.

0.0600 gram ammonia = 0.0494 gram nitrogen = 9.19 per cent. nitrogen.

II. 0.6108 gram material gave :

0.0678 gram ammonia = 0.0559 gram nitrogen = 9.15 per cent. nitrogen.

	Calculated for $\text{ZrCl}_4 \cdot 4\text{C}_6\text{H}_5\text{NH}_2$ .	I. Found.	II.
Chlorine .....	23.49	23.25	23.32
Zirconium .....	14.98	14.83	15.06
Nitrogen .....	9.27	9.19	9.15

Since analysis would show no difference in the composition of  $\text{ZrCl}_4 \cdot 4\text{C}_6\text{H}_5\text{NH}_2$  and a mixture of  $\text{ZrCl}_4(\text{C}_6\text{H}_5\text{NH}_2)_2 + 2\text{C}_6\text{H}_5\text{NH}_2 \cdot \text{HCl}$ , the following method was resorted to in order to prove that it was the first and not the second compound which was formed. The substance, after having been completely freed from aniline, was treated with chloroform, in which it proved to be easily and completely soluble, whereas aniline hydrochloride is insoluble in the same reagent, and hence was not present in the compound. Also no substituted chloraniline,  $\text{C}_6\text{H}_4\text{ClNH}_2$ , could have been formed, as this is soluble in ether, and the existence of no such substance was indicated in the ethereal filtrate. This conclusively proves that the compound is purely additive in nature, and has the formula  $\text{ZrCl}_4 \cdot 4\text{C}_6\text{H}_5\text{NH}_2$ . This same proof may be used as an argument for the additive character of all the zirconium and thorium derivatives described in this research.

*b. Thorium Tetrachloride*,  $\text{ThCl}_4 \cdot 4\text{C}_6\text{H}_5\text{NH}_2$ . — Aniline produced a precipitate slightly gray in color, and soluble in chloroform. Its analysis indicated a formula in correspondence with that of the zirconium derivative.

0.2536 gram material gave :

0.1940 gram silver chloride = 0.0479 gram chlorine = 18.89 per cent. chlorine.

0.0906 gram thorium dioxide = 0.0796 gram thorium = 31.39 per cent. thorium.

0.5536 gram material gave :

0.0488 gram ammonia = 0.0402 gram nitrogen = 7.41 per cent. nitrogen.

	Calculated for $\text{ThCl}_4 \cdot 4\text{C}_6\text{H}_5\text{NH}_2$ .	Found.
Chlorine .....	19.02	18.89
Thorium .....	31.15	31.39
Nitrogen .....	7.61	7.41

*c. Lead Tetrachloride,  $\text{PbCl}_4 \cdot 3\text{C}_6\text{H}_5\text{NH}_2$ .*—Aniline gave a dark green, stable compound with lead tetrachloride in dilute solution. A more concentrated solution of the lead salt reacts very violently with aniline, probably giving rise to the same chlorinated products as tin tetrachloride, such as violaniline, mauvaniline, rosaniline, and triphenylendiamine blue—Girard and Pabst.<sup>1</sup> The dark green compound analyzed for three molecules of aniline.

0.2104 gram material gave :

0.1950 gram silver chloride = 0.0483 gram chlorine = 22.94 per cent. chlorine.

0.2042 gram material gave :

0.0963 gram lead sulphate = 0.0658 gram lead = 32.22 per cent. lead.

0.4012 gram material gave :

0.1929 gram platinum = 0.0277 gram nitrogen = 6.90 per cent. nitrogen.

	Calculated for $\text{PbCl}_4 \cdot 3\text{C}_6\text{H}_5\text{NH}_2$ .	Found.
Chlorine.....	22.61	22.94
Lead .....	32.96	32.22
Nitrogen .....	6.69	6.90

#### F. TOLUIDINE.

*a. Zirconium Tetrachloride,  $\text{ZrCl}_4 \cdot 4\text{C}_6\text{H}_4\text{CH}_3\text{NH}_2$ .*—As aniline gave a derivative with zirconium tetrachloride, toluidine was also tried with like result. Analysis indicated that this compound contained four molecules of toluidine, showing it to be analogous to the aniline derivative.

0.3772 gram material gave :

0.3240 gram silver chloride = 0.0802 gram chlorine = 21.26 per cent. chlorine.

0.0694 gram zirconium dioxide = 0.0512 gram zirconium = 13.60 per cent. zirconium.

0.4296 gram material gave :

0.0456 gram ammonia = 0.0376 gram nitrogen = 8.74 per cent. nitrogen.

<sup>1</sup> *Bull. Soc. Chim.*, 34, 33.

	Calculated for $\text{ZrCl}_4 \cdot 4\text{C}_6\text{H}_4\text{CH}_2\text{NH}_2$ .	Found.
Chlorine.....	21.50	21.26
Zirconium.....	13.72	13.60
Nitrogen.....	8.48	8.74

*b. Thorium Tetrachloride*,  $\text{ThCl}_4 \cdot 3\text{C}_6\text{H}_4\text{CH}_2\text{NH}_2$ .—This was a greenish white precipitate and showed a departure from the other derivatives and from its analogous zirconium compound in that it only contained three molecules of the base.

0.5012 gram material gave :

0.4074 gram silver chloride = 0.1008 gram chlorine = 20.12 per cent. chlorine.

0.1940 gram thorium dioxide = 0.1705 gram thorium = 34.01 per cent. thorium.

0.7500 gram material gave :

0.0526 gram ammonia = 0.0433 gram nitrogen = 5.78 per cent. nitrogen.

	Calculated for $\text{ThCl}_4 \cdot 3\text{C}_6\text{H}_4\text{CH}_2\text{NH}_2$ .	Found.
Chlorine.....	20.41	20.12
Thorium.....	33.44	34.01
Nitrogen.....	6.04	5.78

*c. Lead Tetrachloride*.—With toluidine no additive product could be obtained, even by using quite dilute solutions of lead tetrachloride, as the amine was decomposed, giving a deep purple solution. Hence lead tetrachloride evidently has about the same action on toluidine as bleaching lime or tin tetrachloride.

#### G. PYRIDINE.

As pyridine and quinoline are strong bases, and as they may be considered tertiary amines, it was thought probable that these reagents would form derivatives with the tetrachlorides in a manner similar to aniline and toluidine. Experiment proved this surmise to be a correct one, as a compound was formed in both instances. It may be stated that Classen and Zahorski<sup>1</sup> have obtained compounds of lead tetrachloride with the hydrochlorides of pyridine and quinoline, and they are described as additive products. Goebbles<sup>2</sup> has also obtained compounds of lead tetrachloride with the salts of such complex organic bases as picoline, lutidine and collidine.

<sup>1</sup> *Ztschr. anorg. Chem.*, 4, 100.

<sup>2</sup> *Ber. d. chem. Ges.*, 28, 792.

The compounds of zirconium and thorium tetrachlorides with pyridine and quinoline are light gray to brown flocculent precipitates. Unlike the derivatives with the preceding amines, they appeared to be rather unstable in moist air, in consequence of which considerable difficulty was experienced in obtaining suitable portions for analysis, as the compounds had to be preserved under anhydrous ether.

*a. Zirconium Tetrachloride,  $ZrCl_4 \cdot 2C_5H_5N$ .*—The best analysis that could be obtained for the pyridine derivative approximated to a formula containing two molecules of the base.

0.5420 gram material gave :

0.7805 gram silver chloride = 0.1932 gram chlorine = 35.64 per cent. chlorine.

0.1758 gram zirconium dioxide = 0.1299 gram zirconium = 23.97 per cent. zirconium.

0.6118 gram material gave :

0.0506 gram ammonia = 0.0417 gram nitrogen = 6.83 per cent. nitrogen.

	Calculated for $ZrCl_4 \cdot 2C_5H_5N$ .	Found.
Chlorine.....	36.35	35.64
Zirconium.....	23.19	23.97
Nitrogen .....	7.18	6.83

*b. Thorium Tetrachloride,  $ThCl_4 \cdot C_5H_5N$ .*—0.5002 gram material gave :

0.6270 gram silver chloride = 0.1552 gram chlorine = 31.02 per cent. chlorine.

0.2939 gram thorium dioxide = 0.2583 gram thorium = 51.64 per cent. thorium.

0.4107 gram material gave :

0.0126 gram ammonia = 0.0104 gram nitrogen = 2.53 per cent. nitrogen.

	Calculated for $ThCl_4 \cdot C_5H_5N$ .	Found.
Chlorine.....	31.30	31.02
Thorium .....	51.28	51.64
Nitrogen .....	3.09	2.53

*c. Lead Tetrachloride,  $PbCl_4 \cdot 2C_5H_5N$ .*—Pyridine gave a pale yellow precipitate with lead tetrachloride of much greater stability than the foregoing compounds.

0.2506 gram material gave :

0.2780 gram silver chloride = 0.0688 gram chlorine = 27.46 per cent. chlorine.

0.3125 gram material gave :

0.1842 gram lead sulphate = 0.1258 gram lead = 40.26 per cent. lead.

0.3062 gram material gave :

0.1112 gram platinum = 0.0161 gram nitrogen = 5.21 per cent. nitrogen.

	Calculated for $\text{PbCl}_4 \cdot 2\text{C}_2\text{H}_5\text{N}$ .	Found.
Chlorine.....	28.01	27.46
Lead .....	40.83	40.26
Nitrogen .....	5.52	5.21

#### H. QUINOLINE.

*a. Zirconium Tetrachloride*,  $\text{ZrCl}_4 \cdot 2\text{C}_9\text{H}_7\text{N}$ . — 0.6140 gram material gave :

0.6977 gram silver chloride = 0.1727 gram chlorine = 28.12 per cent. chlorine.

0.1592 gram zirconium dioxide = 0.1177 gram zirconium = 19.17 per cent. zirconium.

0.7226 gram material gave :

0.0478 gram ammonia = 0.0394 gram nitrogen = 5.45 per cent. nitrogen.

	Calculated for $\text{ZrCl}_4 \cdot 2\text{C}_9\text{H}_7\text{N}$ .	Found.
Chlorine.....	28.94	28.12
Zirconium.....	18.47	19.17
Nitrogen .....	5.72	5.45

*b. Thorium Tetrachloride*,  $\text{ThCl}_4 \cdot \text{C}_9\text{H}_7\text{N}$ . — 0.4110 gram material gave :

0.4634 gram silver chloride = 0.1147 gram chlorine = 27.91 per cent. chlorine.

0.2175 gram thorium dioxide = 0.1911 gram thorium = 46.50 per cent. thorium.

0.4212 gram material gave :

0.0129 gram ammonia = 0.0106 gram nitrogen = 2.52 per cent. nitrogen.

	Calculated for $\text{ThCl}_4 \cdot \text{C}_9\text{H}_7\text{N}$ .	Found.
Chlorine.....	28.19	27.91
Thorium .....	46.18	46.50
Nitrogen .....	2.78	2.52

*c. Lead Tetrachloride,  $\text{PbCl}_4 \cdot 2\text{C}_9\text{H}_7\text{N}$ .*—Quinoline reacted very energetically with lead tetrachloride, yielding a lemon-yellow precipitate which proved to be quite stable.

0.3012 gram material gave :

0.2806 gram silver chloride = 0.0695 gram chlorine = 23.06 per cent. chlorine.

0.2298 gram material gave :

0.1140 gram lead sulphate = 0.0779 gram lead = 33.90 per cent. lead.

0.2792 gram material gave :

0.0845 gram platinum = 0.0121 gram nitrogen = 4.34 per cent. nitrogen.

	Calculated for $\text{PbCl}_4 \cdot 2\text{C}_9\text{H}_7\text{N}$ .	Found.
Chlorine.....	23.39	23.06
Lead .....	34.10	33.90
Nitrogen .....	4.61	4.34

#### I. $\beta$ -NAPHTHYLAMINE.

*a. Zirconium Tetrachloride,  $\text{ZrCl}_4 \cdot 2\text{C}_{10}\text{H}_7\text{NH}_2$ .*—On adding a solution of naphthylamine in anhydrous ether to a solution of zirconium tetrachloride a grayish brown precipitate was produced, the analysis of which approximated to the formula given above.

0.5736 gram material gave :

0.6419 gram silver chloride = 0.1589 gram chlorine = 27.70 per cent. chlorine.

0.1397 gram zirconium dioxide = 0.1032 gram zirconium = 18.00 per cent. zirconium.

0.7012 gram material gave :

0.0426 gram ammonia = 0.0351 gram nitrogen = 5.01 per cent. nitrogen.

	Calculated for $\text{ZrCl}_4 \cdot 2\text{C}_{10}\text{H}_7\text{NH}_2$ .	Found.
Chlorine.....	27.38	27.70
Zirconium .....	17.47	18.00
Nitrogen .....	5.41	5.01

*b. Thorium Tetrachloride,  $\text{ThCl}_4 \cdot \text{C}_{10}\text{H}_7\text{NH}_2$ .*—This derivative was grayish white in color and comparatively stable in the air.

0.2582 gram material gave :

0.2844 gram silver chloride = 0.0704 gram chlorine = 27.27 per cent. chlorine.



0.1329 gram thorium dioxide = 0.1168 gram thorium = 45.25 per cent. thorium.

0.6045 gram material gave :

0.0166 gram ammonia = 0.0137 gram nitrogen = 2.27 per cent. nitrogen.

	Calculated for $\text{ThCl}_4 \cdot \text{C}_{10}\text{H}_7\text{NH}_2$	Found.
Chlorine.....	27.43	27.27
Thorium .....	44.94	44.25
Nitrogen .....	2.70	2.27

*c. Lead Tetrachloride,  $\text{PbCl}_4 \cdot \text{C}_{10}\text{H}_7\text{NH}_2$ .*—Naphthylamine gave a dark green precipitate with lead tetrachloride in a dilute solution; in more concentrated solutions the naphthylamine was apparently decomposed.

0.2276 gram material gave :

0.2604 gram silver chloride = 0.0645 gram chlorine = 28.32 per cent. chlorine.

0.3006 gram material gave :

0.1914 gram lead sulphate = 0.1307 gram lead = 43.47 per cent. lead.

0.2416 gram material gave :

0.0544 gram platinum = 0.0079 gram nitrogen = 3.24 per cent. nitrogen.

	Calculated for $\text{PbCl}_4 \cdot \text{C}_{10}\text{H}_7\text{NH}_2$	Found.
Chlorine.....	28.86	28.32
Lead .....	42.07	43.47
Nitrogen .....	2.84	3.24

#### J. ACID AMIDES.

The action of acetamide and benzamide was tried on the solutions of the tetrachlorides, but no compound resulted in any case, the acid amides evidently not being sufficiently basic to form derivatives like the amines.

Diphenylamine was also tried, but it gave no reaction with either the zirconium or thorium salt. The lead salt gave a deep blue solution and lead chloride separated out, showing that the lead tetrachloride in this case acted like bleaching lime on diphenylamine.

## 5. GENERAL REMARKS.

On comparing the derivatives of the three tetrachlorides here used, many similarities will at once be evident. In order to facilitate with such a comparison, it will not be superfluous to present a tabular résumé of the various derivatives herein prepared and described.

	With $ZrCl_4$ mols. amine.	With $ThCl_4$ mols. amine.	With $PbCl_4$ mols. amine.
Ammonia (from solution)....	8	8	4, 2
Ammonia (without heat) .....	2	6	.
Ammonia (with heat).....	4	6	.
Methylamine.....	4	4	4
Ethylamine .....	4	4	4
Propylamine .....	4	4	4
Aniline.....	4	4	3
Toluidine .....	4	3	decomp.
Pyridine .....	2	1	2
Quinoline .....	2	1	2
Naphthylamine .....	2	1	1
Diphenylamine.....	no reaction	no reaction	decomp.
Acid amides .....	no reaction	no reaction	no reaction

Nearly all these derivatives are stable in the air, the only noticeable exceptions being the pyridine, quinoline, and the lower ammonia compounds of zirconium and thorium. None of them show any tendency toward a crystalline structure, but come down as amorphous precipitates resembling hydroxides.

On heating these compounds in the air they readily split up into the amine hydrochloride and the dioxides; with lead, however, lead dichloride is left on ignition. They are also decomposed when treated with water, and the fixed alkalies precipitate the hydroxides of the three metals.

It will also be noticed that the majority of these derivatives seem to obey the law of Remsen in its application to molecular compounds; and the tendency is apparently toward an even number of molecules, though several of the thorium and lead derivatives deviate from this general law in having an odd number of additive molecules.

Two of the chlorine atoms in lead tetrachloride are very loosely combined, splitting off at the slightest disturbance to the chemical equilibrium of the compound; and yet it is of interest to note that the amines seem to fix these two atoms of

chlorine into a more stable form, doubtless due to some peculiar internal linking in the compound. That these two atoms of chlorine are exceedingly active is seen by the behavior of lead tetrachloride with toluidine, where no additive compound could be obtained, as the amine was decomposed even with dilute solutions, giving rise no doubt to complex chlorinated and condensed products. In fact, concentrated solutions of lead tetrachloride will decompose any of the aromatic amines, with the production of blue, purple, and green-colored solutions and resinous products. In this great activity of two of its atoms of chlorine, lead tetrachloride differs widely from the corresponding salts of zirconium and thorium, as these latter show no tendency to break down to lower chlorides.

UNIVERSITY OF PENNSYLVANIA.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,  
No. 33.]

## II. DERIVATIVES OF THE TETRABROMIDES OF ZIRCONIUM AND THORIUM.

BY J. MERRITT MATTHEWS.

Received September 2, 1898.

### I. INTRODUCTION.

THIS investigation was taken up as an adjunct to the preceding research on the derivatives of the tetrachlorides.

Only derivatives with the four most typical amines—ammonia, ethylamine, aniline and pyridine—were prepared, as it was considered needless to extend the investigation further, when the aim was only to prove a general reaction between the amine bases and the tetrahalides of the fourth group.

The anhydrous tetrabromides of zirconium and thorium were prepared in a manner exactly similar to their tetrachlorides, dry bromine vapors in a current of carbon dioxide gas, being substituted for chlorine. Mellis<sup>1</sup> and Troost and Ouvrard.<sup>2</sup>

Owing to the slight solubility of the tetrabromides in any of the usual organic solvents, the reagents in all cases were added to the dry salts, any excess being removed by washing the product so formed with ether.

<sup>1</sup> *Ztschr. Chem.* (2), 6, 296.

<sup>2</sup> *Ann. chim. phys.* (6), 17, 229.

Several attempts were made to prepare the tetrabromide of lead, proceeding in a manner analogous to that used in the preparation of the tetrachloride, but without success.

## 2. THE AMINE DERIVATIVES.

### A. AMMONIA.

*a. Zirconium Tetrabromide,  $ZrBr_4 \cdot 4NH_3$ .*—On passing dry ammonia gas over zirconium tetrabromide at a slightly elevated temperature, a white compound was formed.

0.5186 gram zirconium tetrabromide increased in weight to 0.6035 gram.

0.2246 gram of this compound, on analysis, gave :

0.3511 gram silver bromide = 0.1494 gram bromine = 66.50 per cent. bromine.

0.0584 gram zirconium dioxide = 0.0432 gram zirconium = 19.22 per cent. zirconium.

0.3024 gram material gave :

0.2426 gram platinum = 0.0422 gram ammonia = 13.96 per cent. ammonia.

	Calculated for $ZrBr_4 \cdot 4NH_3$ .	Found.
Bromine.....	66.80	66.50
Zirconium.....	18.96	19.22
Ammonia.....	14.23	13.96
	Gram.	Gram.
Increase in weight.....	0.0861	0.0849

*b. Thorium Tetrabromide,  $ThBr_4 \cdot 3NH_3$ .*—This was prepared in the same manner as the zirconium compound, and was white in color.

0.4712 gram thorium tetrabromide, increased in weight to 0.5119 gram which, on analysis, gave :

0.6491 gram silver bromide = 0.2762 gram bromine = 53.96 per cent. bromine.

0.2273 gram thorium dioxide = 0.1997 gram thorium = 39.01 per cent. thorium.

	Calculated for $ThBr_4 \cdot 3NH_3$ .	Found.
Bromine.....	53.07	53.96
Thorium.....	38.47	39.01
	Gram.	Gram.
Increase in weight.....	0.0435	0.0407

## B. ETHYLAMINE.

*a. Zirconium Tetrabromide*,  $\text{ZrBr}_4 \cdot 4\text{C}_2\text{H}_5\text{NH}_2$ . — 0.2506 gram zirconium tetrabromide, treated with ethylamine, gave 0.3572 gram of a white compound which, on analysis, yielded :

0.4597 gram silver bromide = 0.1956 gram bromine = 54.75 per cent. bromine.

0.0769 gram zirconium dioxide = 0.0569 gram zirconium = 15.92 per cent. zirconium.

	Calculated for $\text{ZrBr}_4 \cdot 4\text{C}_2\text{H}_5\text{NH}_2$ .	Found.
Bromine.....	54.12	54.75
Zirconium.....	15.36	15.92
	Gram.	Gram.
Increase in weight.....	0.1098	0.1066

*b. Thorium Tetrabromide*,  $\text{ThBr}_4 \cdot 4\text{C}_2\text{H}_5\text{NH}_2$ . — 0.3121 gram thorium tetrabromide, treated with ethylamine, gave 0.4098 gram of a white compound which, on analysis, yielded :

0.4246 gram silver bromide = 0.1807 gram bromine = 44.09 per cent. bromine.

0.1502 gram thorium dioxide = 0.1320 gram thorium = 32.21 per cent. thorium.

	Calculated for $\text{ThBr}_4 \cdot 4\text{C}_2\text{H}_5\text{NH}_2$ .	Found.
Bromine.....	43.71	44.09
Thorium.....	31.69	32.21
	Gram.	Gram.
Increase in weight.....	0.1018	0.0977

## C. ANILINE.

*a. Zirconium Tetrabromide*,  $\text{ZrBr}_4 \cdot 4\text{C}_6\text{H}_5\text{NH}_2$ . — 0.2075 gram zirconium tetrabromide, treated with aniline, gave 0.4117 gram of a brownish colored compound which, on analysis, yielded :

0.3821 gram silver bromide = 0.1626 gram bromine = 40.47 per cent. bromine.

0.0631 gram zirconium dioxide = 0.0467 gram zirconium = 11.62 per cent. zirconium.

	Calculated for $\text{ZrBr}_4 \cdot 4\text{C}_6\text{H}_5\text{NH}_2$ .	Found.
Bromine.....	40.83	40.47
Zirconium.....	11.46	11.62
	Gram.	Gram.
Increase in weight.....	0.1911	0.1932

*b. Thorium Tetrabromide*,  $\text{ThBr}_4 \cdot 4\text{C}_6\text{H}_5\text{NH}_2$ . — 0.2214 gram thorium tetrabromide, treated with aniline, gave 0.3675 gram of a brown-colored compound which, on analysis, yielded :

0.3032 gram silver bromide = 0.1290 gram bromine = 35.10 per cent. bromine.

0.1069 gram thorium dioxide = 0.0939 gram thorium = 25.56 per cent. thorium.

	Calculated for $\text{ThBr}_4 \cdot 4\text{C}_6\text{H}_5\text{NH}_2$ .	Found.
Bromine.....	34.63	35.10
Thorium .....	25.11	25.56
	Gram.	Gram.
Increase in weight.....	0.1492	0.1461

#### D. PYRIDINE.

*a. Zirconium Tetrabromide*,  $\text{ZrBr}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$ . — 0.3551 gram zirconium tetrabromide, treated with pyridine, gave 0.3718 gram of a brown compound which, on analysis, yielded :

0.4876 gram silver bromide = 0.2075 gram bromine = 55.82 per cent. bromine.

0.0802 gram zirconium dioxide = 0.0604 gram zirconium = 16.24 per cent. zirconium.

	Calculated for $\text{ZrBr}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$ .	Found.
Bromine.....	56.22	55.82
Zirconium .....	15.95	16.24
	Gram.	Gram.
Increase in weight.....	0.1357	0.1325

*b. Thorium Tetrabromide*,  $\text{ThBr}_4 \cdot \text{C}_5\text{H}_5\text{N}$ . — 0.2817 gram thorium tetrabromide, treated with pyridine, gave 0.3343 gram of a brownish compound which, on analysis, yielded :

0.3960 gram silver bromide = 0.1685 gram bromine = 50.42 per cent. bromine.

0.1412 gram thorium dioxide = 0.1241 gram thorium = 37.11 per cent. thorium.

	Calculated for $\text{ThBr}_4 \cdot \text{C}_5\text{H}_5\text{N}$ .	Found.
Bromine.....	50.71	50.42
Thorium . ....	36.77	37.11
	Gram.	Gram.
Increase in weight.....	0.0403	0.0426

It will be noticed that these derivatives of the tetrabromides

correspond very closely to those of the tetrachlorides of these same elements in the number of molecules of the amine in combination with one molecule of the halogen salt.

It may be remarked that Classen and Zahorski<sup>1</sup> have obtained additive compounds of lead tetrabromide and lead tetraiodide with the hydrobromic and hydriodic acid salts of several of the organic amines, by decomposing the corresponding chlorine compounds with cooled solutions of potassium bromide or potassium iodide. Thus  $\text{PbCl}_4 \cdot 2(\text{C}_6\text{H}_7\text{N} \cdot \text{HCl})$  with potassium bromide gave  $\text{PbBr}_4 \cdot 2(\text{C}_6\text{H}_7\text{N} \cdot \text{HBr})$ , and with potassium iodide,  $\text{PbI}_4 \cdot 2(\text{C}_6\text{H}_7\text{N} \cdot \text{HI})$ .

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### III. THE PREPARATION OF ZIRCONIUM NITRIDES.

By J. MERRITT MATTHEWS.

Received September 2, 1898.

THE ammonia derivative of titanium tetrachloride,  $\text{TiCl}_4 \cdot 4\text{NH}_3$ , when heated in a current of ammonia gas, yields a nitride of titanium; Rose,<sup>2</sup> Persoz.<sup>3</sup> This nitride has been given the formula  $\text{Ti}_3\text{N}_4$ , and has been thoroughly investigated. From this knowledge it was of interest to ascertain if a zirconium nitride could be prepared from its ammonia derivative. The attempt was made and a corresponding zirconium nitride was obtained.

A portion of the zirconium tetrachloride derivative with ammonia,  $\text{ZrCl}_4 \cdot 8\text{NH}_3$ , obtained by passing dry ammonia gas into an ethereal solution of the zirconium salt,<sup>4</sup> was placed in a porcelain boat and gradually heated to redness in a current of nitrogen in a glass combustion tube. Abundant fumes of ammonium chloride were given off and condensed in the cooler part of the tube; the residue left in the boat was pearl-gray in color and in the form of a light powder. On heating this residue in a current of hydrogen, ammonia was evolved, which was conducted into a standardized solution of hydrochloric acid, and thus determined.

<sup>1</sup> *Ztschr. anorg. Chem.*, 4, 100.

<sup>2</sup> *Pogg. Ann.*, 16, 57.

<sup>3</sup> *Ann. chim. phys.*, 44, 321.

<sup>4</sup> This Journal, 20, 821.

When this compound was heated in the air it lost weight, and became pure white in color, passing over into the dioxide,  $\text{ZrO}_2$ , and the zirconium was estimated in this form.

## ANALYSES.

I. 0.2416 gram material gave :

0.0836 gram ammonia = 0.0688 gram nitrogen = 28.47 per cent. nitrogen.

0.0654 gram material gave :

0.0629 gram zirconium dioxide = 0.0465 gram zirconium = 71.10 per cent. zirconium.

II. 0.2006 gram material gave :

0.0691 gram ammonia = 0.0569 gram nitrogen = 28.36 per cent. nitrogen.

0.2572 gram material gave :

0.2469 gram zirconium dioxide = 0.1827 gram zirconium = 71.05 per cent. zirconium.

These analyses show a close approximation to the formula  $\text{Zr}_3\text{N}_8$ .

	Calculated for $\text{Zr}_3\text{N}_8$ .	I.	Found. II.
Zirconium .....	70.82	71.10	71.04
Nitrogen .....	29.18	28.47	28.36

The residue left after heating this nitride in a current of hydrogen, was lead-gray in color and amorphous; it was soluble in hydrofluoric acid, but proved to be insoluble in the other mineral acids. This appearance and behavior leave little doubt but that this residue consists of metallic zirconium, the action of hydrogen being to reduce the nitride to the metal with the formation of ammonia.

In the preparation of the pure nitride care must be exercised in excluding all air from the apparatus, otherwise a mixture of the oxide and nitride will be obtained. In the preparation of the sample used for the above analyses, all the air was first driven out by means of a vigorous current of carbon dioxide gas, after which a current of nitrogen was allowed to pass through the apparatus for two hours before the compound was heated.

$\text{Zr}_3\text{N}_8$ .—This second nitride was prepared by a procedure differing somewhat from that used in the first. Zirconium tetrachloride was placed in a porcelain boat and gradually heated to



redness in a current of dry ammonia gas. By this method the ammonia derivative,  $\text{ZrCl}_4 \cdot 4\text{NH}_3$ , was at first formed.<sup>1</sup> This by the action of heat was broken down into a nitride of zirconium together with the formation of ammonium chloride, which was given off in dense fumes and condensed in the cooler part of the tube, leaving the nitride in the boat in the form of a gray amorphous powder. It was somewhat darker in color than the preceding compound, but resembled it exactly in its behavior. The nitrogen was estimated by heating the compound in a current of hydrogen, and collecting the ammonia evolved in a standardized solution of hydrochloric acid. By heating another portion in the air it became pure white in color, increasing in weight, leaving the dioxide,  $\text{ZrO}_2$ , from the weight of which the zirconium was estimated.

## ANALYSES.

I. 0.2537 gram material gave :

0.0478 gram ammonia = 0.0402 gram nitrogen = 19.23 per cent. nitrogen.

0.2462 gram material gave :

0.2707 gram zirconium dioxide = 0.2001 gram zirconium = 81.27 per cent. zirconium.

II. 0.2217 gram material gave :

0.0523 gram ammonia = 0.0431 gram nitrogen = 19.42 per cent. nitrogen.

0.2546 gram material gave :

0.2792 gram zirconium dioxide = 0.2064 gram zirconium = 81.05 per cent. zirconium.

	Calculated for $\text{Zr}_3\text{N}_8$	Found.	
		I.	II.
Zirconium .....	81.18	81.27	81.05
Nitrogen.....	18.82	19.23	19.42

Mallet<sup>2</sup> obtained a nitride of zirconium by heating the metal in ammonia gas; it is described as a dark gray amorphous powder. A similar product, and one identical, in every way, with that obtained in this present research, was also prepared by Mallet, by heating anhydrous zirconium tetrachloride in ammonia gas. This procedure is exactly similar to that described

<sup>1</sup> This Journal, 20, 823.

<sup>2</sup> *Jsb. Chem.*, 185 145.

above; but Mallet made no investigation into the constitution of the compound which he prepared in this manner.

A nitride of thorium has been prepared by Chydenius<sup>1</sup> by a procedure identical with that used in the preparation of the first zirconium nitride above described. This nitride of thorium is spoken of as a white amorphous powder, and behaves in a manner very similar to the zirconium compound. Thus the analogy existing between these two elements is once more strikingly manifested.

UNIVERSITY OF PENNSYLVANIA.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,  
No. 35.]

#### IV. ON THE SEPARATION OF IRON FROM ZIRCONIUM AND CERTAIN OTHER ALLIED METALS.

BY J. MERRITT MATTHEWS.

Received September 2, 1898.

THOUGH there have been several methods proposed in the past for the separation of iron from zirconium, still chemists have not considered that this problem has, as yet, been satisfactorily solved. All methods which have been recommended for the quantitative separation of these two metals have proved, in some particular, to be untrustworthy, for in all of them traces of iron appear to remain with the zirconium with great pertinacity.

As it may be of interest in connection with the present subject, a brief résumé will here be given of the principal methods which have hitherto been proposed for the separation of iron from zirconium.

Bailey,<sup>2</sup> by the use of a moderately concentrated solution of hydrogen peroxide precipitates  $Zr_2O_3$ , whereas neither iron, aluminum, nor titanium salts are precipitated by this reagent. No accurate results, however, have been worked out by this method.

Berlin<sup>3</sup> observes that if zirconium dioxide, contaminated with iron, is fused with sodium carbonate to a white heat, and the fusion treated with hydrochloric acid, the iron salt dissolves,

<sup>1</sup> *Jsb. Chem.*, 1863, 194.

<sup>2</sup> *J. Chem. Soc.*, 49, 481.

<sup>3</sup> *J. prakt. Chem.*, 58, 147.

leaving the zirconium dioxide undissolved. Scheerer<sup>1</sup> claims that by this fusion a sodium zirconate is formed at first, which is subsequently decomposed on washing with water. Some of the zirconium, however, will go into the solution with the iron; and on the other hand, the zirconium dioxide will still be slightly contaminated with traces of ferric oxide.

Stromeyer<sup>2</sup> applies Chancel's method<sup>3</sup> for the separation of iron from aluminum to its separation from zirconium. By boiling with sodium thiosulphate, zirconium hydroxide is precipitated, while the iron remains in solution. Hermann,<sup>4</sup> however, says that this procedure results in the formation of a zirconium hyposulphite; and traces of iron still continue with the zirconium. For an approximate separation, however, this seems to be a good one.

Rivot<sup>5</sup> recommends the reduction of the iron to the metallic condition, by heating in a current of hydrogen. But it is very doubtful if all of the iron will be eliminated from the zirconium dioxide by this means.

Berthier<sup>6</sup> uses ammonium hydroxide and sulphide, which precipitates ferrous sulphide,  $\text{FeS}$ , and zirconium hydroxide,  $\text{Zr}(\text{OH})_3$ ; when this mixture is treated with sulphurous acid, the ferrous sulphide dissolves; the filtrate may contain some zirconium salt which, on heating, is precipitated from the iron as hydroxide. Hermann claims that this method does not give zirconium dioxide free from iron. Henneberg<sup>7</sup> obtains a zirconium dioxide pure, except in that portion which is precipitated on heating.

Hermann claims to have obtained very pure zirconium dioxide by treating a solution of the chloride with a corresponding amount of ammonium oxalate, and igniting the precipitate. But in this method the amount of zirconium must be known beforehand, in order to calculate the quantity of ammonium oxalate to be added, as any excess of the latter reagent will dissolve the precipitate.

<sup>1</sup> *Pogg. Ann.*, 59, 48.

<sup>2</sup> *Ann. Chem. Pharm.*, 113, 127.

<sup>3</sup> *J. prakt. Chem.*, 74, 471.

<sup>4</sup> *Ibid.*, 97, 340.

<sup>5</sup> *Ann. chim. phys.*, 17, 244.

<sup>6</sup> *Ibid.*, 50, 362.

<sup>7</sup> *J. prakt. Chem.*, 38, 508.

Dubois and Silveria observe that if impure zirconium hydroxide is boiled with oxalic acid, the iron oxalate formed is easily soluble, whereas the zirconium oxalate is insoluble. But Berlin<sup>1</sup> found that the zirconium oxalate is somewhat soluble in oxalic acid, which fact vitiates this method.

Classen<sup>2</sup> gives an electrolytic separation of iron from zirconium; but by his method the zirconium is only determined by difference.

Another method which has been recommended is to boil the impure zirconium salt with a solution of potassium sulphate, when a basic sulphate of zirconium will be precipitated. The precipitation, however, is never complete, as the filtrate always contains some of the zirconium.

It will be seen by this short review that the separation of iron from zirconium is by no means a positive certainty, as there seems to be a great many conflicting opinions entertained by the different authorities.

#### DETAILS OF THE METHOD FOR THE SEPARATION OF IRON FROM ZIRCONIUM.

On introducing a small quantity of water into an ethereal solution of zirconium tetrachloride, it was noticed that a white precipitate was formed, insoluble in excess of ether. This precipitate was no doubt an oxychloride of zirconium, and analyzed in accordance with the well-known hydrated chloride,  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ .

I. 0.1682 gram material gave :

0.1492 gram silver chloride = 21.93 per cent. chlorine.

0.0645 gram zirconium dioxide = 28.34 per cent. zirconium.

II. 0.1276 gram material gave :

0.1181 gram silver chloride = 21.86 per cent. chlorine.

0.0488 gram zirconium dioxide = 28.26 per cent. zirconium.

	Calculated for $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ .	Found.	
		I.	II.
Chlorine.....	22.05	21.93	21.86
Zirconium .....	28.18	28.34	28.26

On testing this precipitate with a solution of potassium thiocyanate, not a trace of iron was indicated, although the zir-

<sup>1</sup> *J. prakt. Chem.*, 58, 145.

<sup>2</sup> *Ber. d. chem. Ges.*, 14, 2783.

conium tetrachloride used in the solution showed a decided contamination by iron under the same conditions.

With this sharp distinction in solubilities of the hydrated salts of zirconium and iron in ether as a basis, a simple and accurate separation of these two elements was immediately suggested.

Weighed quantities of the chlorides of zirconium and iron were mixed together. Previous analyses of these salts were made in order to determine their respective percentages of zirconium and iron. The mixed salts were dissolved in water and carefully evaporated to dryness on a water-bath; after cooling they were treated with absolute ether, and dry hydrochloric acid gas was passed through the liquid. Experience proved that this latter treatment was necessary to effect a rapid and complete solution of the iron salt by the ether, as the ferric chloride on evaporation to dryness evidently forms basic compounds of indefinite composition which are difficultly soluble in ether. The solution was rapidly filtered, and the residue washed with absolute ether several times to insure the removal of the last traces of the iron salt. The residue was then dissolved in water, and the zirconium determined by precipitation as hydroxide by means of ammonium hydroxide; drying the precipitate, igniting and weighing as zirconium dioxide,  $ZrO_2$ . The ether was evaporated or distilled from the filtrate, and the residue dissolved in water, with the addition of a few drops of hydrochloric acid if necessary; and the iron was determined by precipitation with ammonium hydroxide, drying the precipitate, igniting, and weighing as ferric oxide,  $Fe_2O_3$ .

On testing the aqueous solution of the residue containing the zirconium with potassium thiocyanate solution, not a trace of iron was discovered, showing that the separation had been a complete and successful one.

Several analyses were made, using varying relative amounts of the zirconium and iron salts.

I. 0.1824 gram ferric chloride with 0.1262 gram zirconium tetrachloride gave:

0.0540 gram ferric oxide = 29.50 per cent. ferric oxide.

0.0615 gram zirconium dioxide = 48.89 per cent. zirconium dioxide.

II. 0.1763 gram ferric chloride with 0.1890 gram zirconium tetrachloride gave :

0.0524 gram ferric oxide = 29.55 per cent. ferric oxide.

0.0920 gram zirconium dioxide = 48.83 per cent. zirconium dioxide.

III. 0.3064 gram ferric chloride with 0.1620 gram zirconium tetrachloride gave :

0.0910 gram ferric oxide = 29.60 per cent. ferric oxide.

0.0788 gram zirconium dioxide = 48.79 per cent. zirconium dioxide.

IV. 0.6564 gram ferric chloride with 0.2544 gram zirconium tetrachloride gave :

0.1931 gram ferric oxide = 29.36 per cent. ferric oxide.

0.1240 gram zirconium dioxide = 48.78 per cent. zirconium dioxide.

V. 0.1276 gram ferric chloride with 0.6924 gram zirconium tetrachloride gave :

0.0390 gram ferric oxide = 29.70 per cent. ferric oxide.

0.3385 gram zirconium dioxide = 49.04 per cent. zirconium dioxide.

On analyzing the ferric chloride used it gave 29.44 per cent. ferric oxide, while the zirconium chloride gave 48.97 per cent. zirconium dioxide. The latter salt also showed a contamination by iron equivalent to 0.16 per cent. ferric oxide, and in the percentages given in the above analyses, an allowance is made for this correction.

	Used.	I.	II.	Found. III.	IV.	V.
Ferric oxide.....	29.44	29.50	29.55	29.60	29.36	29.70
Zirconium dioxide .	48.97	48.89	48.83	48.79	48.78	49.04

In making a practical use of this separation it is only necessary to obtain the two metals in solution in the form of chlorides and then the details as already given may be applied.

#### ON THE DELICACY OF THE SEPARATION OF IRON FROM ZIRCONIUM.

The fact that zirconium oxychloride is perfectly white in color should not be taken as a final indication that it is absolutely free from traces of iron ; and this should be borne in mind in the preparation of salts for atomic weight determinations. In order

to establish the accuracy of the method which has been described for the separation of iron from zirconium, a series of delicate experiments was carried out with the object of determining approximately the quantity, if any, of iron still remaining with the zirconium salt.

Zirconium tetrachloride, contaminated with iron, was treated with a little water in order to convert it into the oxychloride; it was then digested with ether, and a drop of hydrochloric acid added. The ether was filtered off and the perfectly white residue of zirconium oxychloride was washed several times with absolute ether to insure the removal of the last traces of the iron salt.

A solution of ferric chloride was made, one cc. of which contained 0.000001 gram ferric chloride. This was called solution No. 1.

Another solution of ferric chloride was made, one cc. of which contained 0.0000005 gram ferric chloride. This was called solution No. 2.

One cc. of solution No. 1 was placed in a test-tube, and to this were added one cc. of hydrochloric acid (sp. gr. 1.17), and one cc. of a solution of ten grams ammonium thiocyanate in 100 cc. of water, and the volume of the liquid was made up to ten cc. A slight pink color was noticed. One cc. of solution No. 2 was treated in the same manner, and a just perceptible pink tinge was observed.

One-tenth gram of zirconium tetrachloride was dissolved in five cc. of water, and treated as above; a dark red color immediately appeared.

One-tenth gram of the zirconium oxychloride as freed from iron, was dissolved in five cc. of water, and treated in a similar manner; a very slight pink tinge was perceptible. On comparing this with solutions No. 1 and No. 2, it was found that the intensity of coloration of the zirconium oxychloride solution was between that of the two iron solutions. From this it is to be concluded that the ratio between the amount of iron salt and that of the zirconium salt present in the zirconium oxychloride is approximately between the limits of 1 : 200,000 and 1 : 100,000.

The tetrachloride of zirconium, before its separation from iron, showed a percentage of the latter equivalent to about 0.16

per cent. ferric oxide. By the above comparison this percentage appears to be reduced to something approximately between the limits of 0.001 and 0.0005 per cent. The solution of hydrochloric acid used in these experiments was purified to such an extent that one cc., when treated with one cc. of the ammonium thiocyanate solution, on dilution to ten cc. gave no perceptible pink coloration.

The observations of those delicate tints were made immediately after mixing the solutions, and by comparison with an equal volume of distilled water. On standing for a time the colors were apparently discharged.

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As thorium, cerium, and titanium belong to the same group as zirconium, and form corresponding hydrated oxychlorides insoluble in ether, the same method was applied in the separation of iron from these metals as with zirconium, and very good results were obtained. The method was carried out in every particular as already described, and was also extended to include lanthanum, neodymium, and praseodymium, as their hydrated chlorides were found to be insoluble in ether.

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#### THORIUM FROM IRON.

The thorium salt used was the chloride, and its analysis gave 60.79 per cent. thorium dioxide, and was not appreciably contaminated with iron, so no correction was necessary in the percentages found.

I. 0.5608 gram thorium tetrachloride with 0.2246 gram ferric chloride gave :

0.3418 gram thorium dioxide = 60.95 per cent. thorium dioxide.

0.0657 gram ferric oxide = 29.25 per cent. ferric oxide.

II. 0.2681 gram thorium tetrachloride with 0.4625 gram ferric chloride gave :

0.1628 gram thorium dioxide = 60.72 per cent. thorium dioxide.

0.1364 gram ferric oxide = 29.53 per cent. ferric oxide.

III. 0.5072 gram thorium tetrachloride with 0.3217 gram ferric chloride gave :



0.3075 gram thorium dioxide = 60.63 per cent. thorium dioxide.

0.0952 gram ferric oxide = 29.59 per cent. ferric oxide.

IV. 1.0368 grams thorium tetrachloride with 0.7241 gram ferric chloride gave :

0.6318 gram thorium dioxide = 60.94 per cent. thorium dioxide.

0.2137 gram ferric oxide = 29.51 per cent. ferric oxide.

V. 0.1193 gram thorium tetrachloride with 0.6976 gram ferric chloride gave :

0.0720 gram thorium dioxide = 60.35 per cent. thorium dioxide.

0.2062 gram ferric oxide = 29.58 per cent. ferric oxide.

	Used.	I.	II.	Found. III.	IV.	V.
Ferric oxide .....	29.44	29.25	29.53	29.59	29.51	29.58
Thorium dioxide...	60.79	60.95	60.72	60.63	60.94	60.35

#### CERIUM FROM IRON.

Cerium chloride was used, and its analysis gave 61.11 per cent. cerium dioxide.

I. 0.1098 gram cerium chloride with 0.3510 gram ferric chloride gave :

0.0669 gram cerium dioxide = 60.93 per cent. cerium dioxide.

0.1044 gram ferric oxide = 29.74 per cent. ferric oxide.

II. 0.1930 gram cerium chloride with 0.2574 gram ferric chloride gave :

0.1178 gram cerium dioxide = 61.04 per cent. cerium dioxide.

0.0758 gram ferric oxide = 29.45 per cent. ferric oxide.

III. 0.2240 gram cerium chloride with 0.2642 gram ferric chloride gave :

0.1367 gram cerium dioxide = 61.03 per cent. cerium dioxide.

0.0784 gram ferric oxide = 29.67 per cent. ferric oxide.

IV. 0.7532 gram cerium chloride with 0.1024 gram ferric chloride gave :

0.4598 gram cerium dioxide = 61.05 per cent. cerium dioxide.

0.0301 gram ferric oxide = 29.39 per cent. ferric oxide.

V. 0.1262 gram cerium chloride with 0.8436 gram ferric chloride gave :

0.0774 gram cerium dioxide = 61.33 per cent. cerium dioxide.

0.2489 gram ferric oxide = 29.52 per cent. ferric oxide.

	Used.	I.	II.	Found. III.	IV.	V.
Ferric oxide .....	29.44	29.74	29.45	29.67	29.39	29.52
Cerium dioxide ....	61.11	60.93	61.04	61.03	61.05	61.33

#### TITANIUM FROM IRON.

Titanium chloride was the salt used, and on analysis this gave 57.17 per cent. titanium dioxide.

I. 0.1060 gram titanium chloride with 0.2224 gram ferric chloride gave :

0.0604 gram titanium dioxide = 56.98 per cent. titanium dioxide.

0.0660 gram ferric oxide = 29.68 per cent. ferric oxide.

II. 0.2588 gram titanium chloride with 0.2508 gram ferric chloride gave :

0.1474 gram titanium dioxide = 56.95 per cent. titanium dioxide.

0.0736 gram ferric oxide = 29.35 per cent. ferric oxide.

III. 0.6532 gram titanium chloride with 0.1086 gram ferric chloride gave :

0.3728 gram titanium dioxide = 57.08 per cent. titanium dioxide.

0.0318 gram ferric oxide = 29.28 per cent. ferric oxide.

IV. 0.3549 gram titanium chloride with 0.7643 gram ferric chloride gave :

0.2033 gram titanium dioxide = 57.28 per cent. titanium dioxide.

0.2253 gram ferric oxide = 29.48 per cent. ferric oxide.

V. 0.1083 gram titanium chloride with 0.9212 gram ferric chloride gave :

0.0617 gram titanium dioxide = 56.97 per cent. titanium dioxide.

0.2720 gram ferric oxide = 29.53 per cent. ferric oxide.

	Used.	I.	II.	Found. III.	IV.	V.
Ferric oxide .....	29.44	29.68	29.35	29.28	29.48	29.53
Titanium dioxide ..	57.17	56.98	56.95	57.08	57.28	56.97

## LANTHANUM FROM IRON.

The lanthanum chloride used in the analyses gave 50.20 per cent. lanthanum oxide,  $\text{La}_2\text{O}_3$ .

I. 0.2968 gram lanthanum chloride with 0.1465 gram ferric chloride gave :

0.1485 gram lanthanum oxide,  $\text{La}_2\text{O}_3$ , = 50.03 per cent. lanthanum oxide.

0.0435 gram ferric oxide = 29.69 per cent. ferric oxide.

II. 0.4541 gram lanthanum chloride with 0.7105 gram ferric chloride gave :

0.2274 gram lanthanum oxide,  $\text{La}_2\text{O}_3$ , = 50.08 per cent. lanthanum oxide.

0.2098 gram ferric oxide = 29.53 per cent. ferric oxide.

III. 0.1079 gram lanthanum chloride with 0.6514 gram ferric chloride gave :

0.0539 gram lanthanum oxide,  $\text{La}_2\text{O}_3$ , = 49.95 per cent. lanthanum oxide.

0.1926 gram ferric oxide = 29.57 per cent. ferric oxide.

IV. 0.7525 gram lanthanum chloride with 0.1024 gram ferric chloride gave :

0.3769 gram lanthanum oxide,  $\text{La}_2\text{O}_3$ , = 50.09 per cent. lanthanum oxide.

0.0304 gram ferric oxide = 29.68 per cent. ferric oxide.

V. 0.5048 gram lanthanum chloride with 0.5025 gram ferric chloride gave :

0.2539 gram lanthanum oxide,  $\text{La}_2\text{O}_3$ , = 50.30 per cent. lanthanum oxide.

0.1485 gram ferric oxide = 29.55 per cent. ferric oxide.

	Used.	I.	II.	Found. III.	IV.	V.
Ferric oxide .....	29.44	29.69	29.54	29.57	29.68	29.55
Lanthanum oxide, $\text{La}_2\text{O}_3$ .....	50.20	50.03	50.08	49.95	50.09	50.30

## PRASEODYMIUM FROM IRON.

The salt used was praseodymium nitrate, and its analysis gave 43.33 per cent. praseodymium oxide,  $\text{Pr}_2\text{O}_3$ .

I. 0.5308 gram praseodymium nitrate with 0.4245 gram ferric chloride gave :

0.2293 gram praseodymium oxide,  $\text{Pr}_2\text{O}_3$ , = 43.20 per cent. praseodymium oxide.

0.1261 gram ferric oxide = 29.70 per cent. ferric oxide.

II. 0.5090 gram praseodymium nitrate with 0.3596 gram ferric chloride gave :

0.2198 gram praseodymium oxide,  $\text{Pr}_2\text{O}_3$ , = 43.18 per cent. praseodymium oxide.

0.1064 gram ferric oxide = 29.59 per cent. ferric oxide.

III. 0.1085 gram praseodymium nitrate with 0.7240 gram ferric chloride gave :

0.0465 gram praseodymium oxide,  $\text{Pr}_2\text{O}_3$ , = 42.86 per cent. praseodymium oxide.

0.2139 gram ferric oxide = 29.54 per cent. ferric oxide.

IV. 0.6849 gram praseodymium nitrate with 0.1096 gram ferric chloride gave :

0.2960 gram praseodymium oxide,  $\text{Pr}_2\text{O}_3$ , = 43.33 per cent. praseodymium oxide.

0.0323 gram ferric oxide = 29.43 per cent. ferric oxide :

V. 0.2532 gram praseodymium nitrate with 0.2485 gram ferric chloride gave :

0.1092 gram praseodymium oxide,  $\text{Pr}_2\text{O}_3$ , = 43.13 per cent. praseodymium oxide.

0.0735 gram ferric oxide = 29.58 per cent. ferric oxide.

	Used.	I.	II.	Found. III.	IV.	V.
Ferric oxide .....	29.44	29.70	29.59	29.54	29.43	29.58
Praseodymium oxide, $\text{Pr}_2\text{O}_3$ ...	43.33	43.20	43.18	42.86	43.22	43.13

#### NEODYMIUM FROM IRON.

Neodymium nitrate was used, and its analysis gave 42.20 per cent. neodymium oxide,  $\text{Ne}_2\text{O}_3$ .

I. 0.1763 gram neodymium nitrate with 0.4286 gram ferric chloride gave :

0.0740 gram neodymium oxide,  $\text{Ne}_2\text{O}_3$ , = 41.97 per cent. neodymium oxide.

0.1261 gram ferric oxide = 29.42 per cent. ferric oxide.

II. 0.6389 gram neodymium nitrate with 0.1842 gram ferric chloride gave :

0.2688 gram neodymium oxide,  $\text{Ne}_2\text{O}_3$ , = 42.07 per cent. neodymium oxide.

0.0540 gram ferric oxide = 29.32 per cent ferric oxide.

III. 0.7246 gram neodymium nitrate with 0.7562 gram ferric chloride gave :

0.3051 gram neodymium oxide,  $\text{Ne}_2\text{O}_3$ , = 42.11 per cent. neodymium oxide.

0.2229 gram ferric oxide = 29.48 per cent. ferric oxide.

IV. 0.1545 gram neodymium nitrate with 0.2046 gram ferric chloride gave :

0.0645 gram neodymium oxide,  $\text{Ne}_2\text{O}_3$ , = 41.75 per cent. neodymium oxide.

0.0610 gram ferric oxide = 29.81 per cent. ferric oxide.

V. 0.2081 gram neodymium nitrate with 0.7680 gram ferric chloride gave :

0.0869 gram neodymium oxide,  $\text{Ne}_2\text{O}_3$ , = 41.76 per cent. neodymium oxide.

0.2271 gram ferric oxide = 29.57 per cent. ferric oxide.

	Used.	I.	II.	Found. III.	IV.	V.
Ferric oxide .....	29.44	29.42	29.32	29.48	29.81	29.57
Neodymium oxide, $\text{Ne}_2\text{O}_3$ , .....	42.20	41.97	42.07	42.11	41.75	41.76

The praseodymium and neodymium salts existing originally as nitrates, were evaporated to dryness with hydrochloric acid in order to convert them into the chloride form.

#### GENERAL REMARKS.

Gooch and Havens, in the *American Journal of Science* for December, 1896, describe a method for the separation of aluminum from iron by treatment with anhydrous ether saturated with hydrochloric acid gas. The hydrated chloride of aluminum remains insoluble, whereas the ferric salt is completely dissolved. This method is practically the same as the one herein described for the separation of iron from zirconium and the other rare earths ; but the results of this present research were mostly obtained in October and November, 1896, before the writer was aware of the contemporaneous work of Gooch and

Havens. These latter writers also describe a separation of aluminum from glucinum by the same method.<sup>1</sup>

The use of absolute ether may militate somewhat against the practical application of this method to general analytical purposes; since in the case of most of the metals experimented upon, very good separations are already known which do not require the use of a reagent both difficult and unpleasant to manipulate. This method, however, is especially recommended for the separation of iron from zirconium, the separations of the other metals being only tried as a matter of interest through the analogy existing between those metals and zirconium. A point, however, which may prove of practical importance, and which it is most desirable to emphasize here, is that by carefully following out the procedure herein described, zirconium oxychloride and dioxide may be easily and quickly prepared perfectly free from iron. This fact may be of considerable importance and utility in the preparation of zirconium compounds for use in atomic weight determinations, where a high degree of purity is absolutely necessary in order to obtain authentic results.

UNIVERSITY OF PENNSYLVANIA.

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[CONTRIBUTION FROM THE LABORATORY OF THE NORTH DAKOTA AGRICULTURAL COLLEGE, NO. I.]

### THE PROTEIDS OF CREAM.

BY E. F. LADD.

Received September 28, 1898.

**I**N some preliminary work in the chemistry of ripening cream for butter-making, several methods for the separation of proteids were tried, some of which were not suited to this work, and the results may be of interest, if not of value, to other workers in the same line. In the work here presented it was not our purpose to determine each of the individual proteids that cream might contain, but rather to learn something of the changes that take place in the proteids of cream during the process of ripening.

For our purpose the proteids of milk were divided into four groups, casein, albumen, albumoses, and peptones; that is, the

<sup>1</sup> *Am. J. Sci.*, August, 1897.

methods employed brought down whatever of proteids were present in one of these four groups, and no attempt was made to determine the globulins, etc. The methods employed for the separation of these groups were as follows:

*Casein*.—About ten grams of cream were diluted with eighty cc. of water and three cc. of a saturated alum solution added, the whole well stirred and then allowed to stand for ten minutes, then filtered and washed with hot water and the nitrogen determined in the residue by means of the Kjeldahl method.

Acetic acid was first employed as the precipitant for casein. This worked well on fresh cream, but on the ripened and sour cream no concordant results could be depended on and the filtration was very difficult.

*Albumen*.—The filtrate from the casein was then heated to boiling, allowed to stand for a few minutes, then filtered and washed with hot water and the nitrogen determined as in casein. Other methods were tried, such as tannin solution, sodium chloride, and tannic acid, but these methods were not found suited for the separation of albumen in the presence of proteoses, although in other lines of work they gave fairly good results.

*Albumoses*.—The filtrate from the last was evaporated to a small bulk, say fifty to sixty cc., and the solution then saturated with zinc sulphate. After standing for ten to twelve hours it was filtered, the precipitate well washed, and the nitrogen determined as before.

For separating albumoses, ammonium sulphate was first employed, but with a product like milk or cream, we found it impossible to make quantitative separations by means of this reagent, as it was impossible to get rid of all traces of salt without losing a considerable per cent. of the albumoses themselves. The method proved valuable, however, for separating quantities for dialyses to be purified and used in proximate analyses, or for further separating into the several albumoses.

*Peptones*.—The filtrate from the above was then evaporated to a small bulk, removing thereby a portion of the zinc salt and absolute alcohol to eighty per cent. of the volume added. After standing twelve hours, filtering and washing with alcohol, the nitrogen was determined.

Further experiments are necessary to determine whether the filtrate may be safely concentrated for the peptones without any loss of proteids. The loss in this case could have been but little, if any, but some work with urines indicated that a loss might result. This point will be further tested. The total nitrogen having been previously determined in the cream, we have a check on our work, and in our studies the sum of the nitrogen in the several precipitates have agreed very closely with the total nitrogen in the cream. Having found methods that would give fairly close results on known products, we next proceeded to determine the changes in the proteids of cream during the process of ripening.

A large number of determinations were made, always with about the same general results, therefore two cases will suffice for this study. No. 1 is for a fresh cream but four hours from time of drawing the milk from the cow's udder. The cream was separated by means of the centrifugal separator.

No. 2 is for a sample of cream well ripened, quite sour and ready for churning. The per cent. of nitrogen is given in each case.

	No. 1. Fresh. Per cent.	No. 2. Ripened. Per cent.
Nitrogen in casein.....	0.237	0.249
"    "    albumen .....	0.035	0.027
"    "    albumoses .....	0.031	0.033
"    "    peptones .....	0.023	0.032
Total nitrogen.....	0.326	0.341
Total nitrogen in cream.....	0.335	0.344
Loss.....	0.009	0.003

From the above it will be seen that the loss in working by these methods was not great, and further that there is not a very marked change in the proteids of cream during the process of ripening. Further studies may show that the product precipitated as casein in case of the ripened cream differs somewhat from that precipitated from the fresh cream. Such seemed to be the case, but the purified product from fresh and ripened cream has not been fully studied. Further results, together with other studies in milk and cream, will be given later in the form of a station publication.



[CONTRIBUTION FROM THE LABORATORY OF THE NORTH DAKOTA AGRICULTURAL COLLEGE, No. 2.]

## HUMATES AND SOIL FERTILITY.

BY E. F. LADD.

Received September 26, 1898.

PREVIOUS to the time of Liebig it was quite generally supposed that plants derive their food principally from the humus of the soil, but after Liebig showed that the greater part of plant food was derived from the atmosphere, humus received less attention at the hands of chemists and other investigators, possibly less than it deserved. Agriculturists, however, have assigned a high place to humus in the soil, recognizing that it played an important part in modifying the physical conditions of the soil, in relation of soils to the water content as well as to the soil temperature. Chemists gave so little attention to this that in soil analyses humus has not been generally estimated, and almost no determinations have been made of the relation of humus to the mineral matter, or in other words the amounts and kinds of mineral constituents contained in the humates, or whether any relation existed between the amount of phosphates, potash, lime, and nitrogen contained in the soil humates and the productivity of the soil. We do not even know what humus is except that it is a very complex product. It would seem that a product so highly prized by the farmer as a constituent of his soil, should be worthy of most careful study. Snyder has given considerable attention to the subject of humus in the soil and humus products. In this article an attempt will be made to trace a relationship between the humates and soil fertility, and to show the necessity for a fuller consideration of the humates by the soil analyst. Although my own observations and experiments have extended over a period of eight years and many determinations have been made at different dates during this time, as other duties have permitted, work in this field has only just reached the point of showing where work must begin without having accomplished anything definite more than a strong conviction of the necessity for a most careful and painstaking investigation

of the humus question, especially in any investigation of the soils of North Dakota.

If by placing on record at this time the data secured during the past few months other workers are interested in soils and induced to take up the work, I shall have accomplished my object. The study of data presented by different workers will enable us to determine what are general principles and what results peculiar to local conditions. The soils of North Dakota contain such quantities of humus and organic matter that many problems can only be studied on soils from other places in order to determine some of the most important facts in connection with the humus problem.

In the following table are given results for twenty-four samples of soils, showing the per cent. of humates and humus, also the per cent. of total phosphates, lime, potash, and nitrogen contained in the soil, together with the amounts extracted as humates.

Soil.			Nitrogen.		Phosphoric acid, $P_2O_5$ .		Lime, CaO.		Potash, $K_2O$ .	
	Humates.	Humus.	Total.	In humus.	Total.	In humus.	Total.	In humus.	Total.	In humus.
411	6.85	4.03	0.340	0.163	0.29	0.086	0.58	0.336	0.32	0.110
413	9.20	4.45	0.390	0.193	0.37	0.168	0.37	0.263	0.51	0.201
414	5.92	2.54	0.190	0.152	0.16	0.097	0.40	0.210	0.21	0.083
415	8.02	3.94	0.200	0.140	0.30	lost	0.80	lost	0.30	lost
416	8.86	3.66	0.300	0.146	0.26	0.184	2.48	0.680	0.18	0.089
417	5.37	3.20	0.310	0.152	0.29	0.116	0.94	0.453	0.19	0.136
419	7.42	4.06	0.345	0.105	0.27	0.161	2.70	0.159	0.42	0.139
420	3.84	1.56	0.187	0.041	0.37	0.179	2.10	0.892	0.22	0.075
421	4.27	2.53	0.234	0.094	0.31	0.192	2.00	1.030	0.18	0.089
422	5.79	4.10	0.218	0.111	0.27	0.199	1.25	1.010	0.45	....
423	15.26	7.73	0.390	0.176	0.33	0.132	0.83	0.370	0.44	0.200
424	14.57	7.25	0.250	0.152	0.38	0.184	0.80	0.420	0.60	0.204
425	14.81	7.90	0.300	0.176	0.40	0.143	0.86	0.343	0.73	0.200
426	14.20	7.86	0.396	0.175	0.38	0.117	1.01	0.476	0.54	0.200
427	14.65	7.01	0.300	0.133	0.39	0.139	0.85	0.429	0.63	0.233
428	14.81	6.92	0.456	0.183	0.39	0.161	1.05	0.389	0.50	0.180
270a	7.40	4.78	0.220	0.157	0.14	0.110	trace	0	0.44	....
270b	7.32	4.18	0.310	0.256	0.24	0.137	0.64	0.423	0.25	....
86a	7.57	4.21	0.250	0.169	0.18	0.120	0.47	0.209	0.55	....
86b	5.85	3.33	0.180	0.123	0.20	0.103	0.34	0.170	0.35	....
277a	9.99	6.43	0.360	0.284	0.16	0.092	0.33	0.186	0.23	....
277b	11.10	4.89	0.450	0.362	trace	trace	1.12	0.609	0.42	....
81a	7.65	4.20	0.250	0.170	0.18	0.117	0.91	0.513	0.59	....
81b	8.94	3.80	0.180	0.115	0.20	0.225	0.79	0.453	0.58	....

The soils examined were from various parts of the state, mostly outside of the valley, excepting 423 to 428 inclusive, which were

from the agricultural college farm, and represent principally soils from the plots where crop rotation experiments are being conducted. It will be seen that there is quite a range of variation for the different constituents in the twenty-four samples. This variation may best be shown in tabular form.

In twenty-four samples.	Humus.	Humates.	Nitrogen.		Phosphoric acid, $P_2O_5$ .		Lime, CaO.		Potash, $K_2O$ .	
			Total.	In humus.	Total.	In humus.	Total.	In humus.	Total.	In humus.
Minimum.	3.84	1.56	0.180	0.041	trace	0.086	trace	0	0.18	0.075
Maximum	15.26	7.90	0.456	0.362	0.40	0.199	2.70	1.03	0.73	0.233
Average ..	9.15	4.77	0.292	0.163	0.269	0.138	0.944	0.436	0.409	0.153

Phosphoric acid for 81*b* has been excluded, as evidently there is an error in one of the sets of determinations, although good duplicates are shown for each set. From this table it is evident that there is quite a range of mineral matter in the humates, and that a varying proportion of these constituents exist in the humates as compared with the total in the soil. The next table shows the per cent. of these several constituents that existed in the humates as compared with the total in the soil.

## PER CENT. OF THE TOTAL IN THE HUMATES.

Number.	Nitrogen.	Phosphate, $P_2O_5$ .	Lime, CaO.	Potash, $K_2O$ .	Humus.
411	47.9	29.7	57.9	34.3	58.9
413	49.5	45.4	71.1	39.4	48.3
414	80.0	60.6	52.5	39.5	42.9
415	70.0	...	...	...	49.1
416	48.6	70.7	27.4	49.4	41.3
417	49.0	40.0	48.0	71.6	59.5
419	30.4	59.6	5.88	33.1	54.7
420	21.9	45.9	42.4	34.1	40.6
421	40.1	61.9	51.5	49.4	59.2
422	50.9	73.6	80.8	...	70.8
423	45.1	40.0	44.6	45.4	51.3
424	60.8	48.4	52.5	34.0	49.7
425	58.6	35.7	39.8	27.4	53.4
426	44.4	30.8	47.1	37.0	55.3
427	44.3	35.6	40.4	36.9	47.8
428	40.1	41.3	37.0	36.0	46.7
270a	71.3	78.6	0	...	64.6
270b	82.5	56.9	66.1	...	57.1
86a	67.6	66.6	44.5	...	55.6
86b	68.3	51.5	50.0	...	56.9
277a	78.9	57.5	56.3	...	64.6
277b	80.4	trace	54.4	...	44.0
81a	68.0	65.0	56.3	...	56.2
81b	63.9	112(?)	57.3	...	42.5
Average	55.8	51.3	46.2	37.4	52.1

If we represent the figures given in a form to show the amounts per acre, assuming that one acre of soil to the depth of one foot weighs 2,225,000 pounds, then for nitrogen we have :

NITROGEN PER ACRE.		
	Total in soil. Pounds.	In humus. Pounds.
Highest .....	10,146	8,054
Lowest .....	4,005	912
	<hr/>	<hr/>
Average .....	6,497	3,627

In the same manner excluding the soil when there was almost an absence of phosphates, we have for phosphoric acid :

PHOSPHORIC ACID ( $P_2O_5$ ) PER ACRE.		
	Total in soil. Pounds.	In humus. Pounds.
Highest .....	8,900	4,428
Lowest .....	3,115	1,913
	<hr/>	<hr/>
Average .....	5,985	3,061

Here we find marked differences, and when we come to study the character of the humus itself, we find other conditions not yet understood, and which we do not care to consider at the present time. The unqualified term *humus* conveys but little more meaning than the term soil without any specifications as to kind and properties.

#### INFLUENCE OF CONTINUOUS CROPPING.

A field that has been continuously cropped for seventeen years in succession, occasionally to oats, but principally to wheat, began to show a marked decrease in yield. The soil is quite light, containing considerable sand, in fact it would be classed as a sandy loam. A field adjoining had never been broken, and originally the two fields were alike in general appearance, as I am informed by the proprietor. The ordinary soil analyses gave results as follows :

	Old soil. Cropped seventeen years. No. 420.	New soil. Unbroken prairie. No. 421.
Moisture .....	2.76	2.74
Sand, silica, etc.....	72.58	75.50
Soluble silica, $\text{SiO}_2$ .....	11.73	9.65
Volatile matter.....	5.26	6.30
Potash, $\text{K}_2\text{O}$ .....	0.22	0.18
Soda, $\text{Na}_2\text{O}$ .....	0.42	0.66
Lime, $\text{CaO}$ .....	2.10	2.00
Magnesia, $\text{MgO}$ .....	0.08	0.07
Manganese, $\text{Mn}_2\text{O}_3$ .....	trace	trace
Iron, $\text{Fe}_2\text{O}_3$ .....	0.22	0.20
Alumina, $\text{Al}_2\text{O}_3$ .....	3.41	2.19
Phosphoric acid, $\text{P}_2\text{O}_5$ .....	0.37	0.31
Sulphuric acid, $\text{SO}_3$ .....	0.79	0.72
Nitrogen .....	0.187	0.234

Until the last three or four crops the field had been a good producer, and an examination of the results above indicates very little as to the probable reason for the loss of productive power. The nitrogen is lower than the average for the state, but no lower than for the same group of soils in the state, and not nearly so low as in many fertile soils from other states. Of phosphates there is a good supply. Taking all things into consideration, I should find it difficult, if not quite impossible from the above analyses, to determine which field had been longest cropped.

An examination for the soil humus was then made with results as follows :

## PER CENT.

	Old soil. No. 420.	New soil. No. 421.
Humates .....	3.04	4.27
Humus .....	1.56	2.53
Phosphoric acid, $\text{P}_2\text{O}_5$ .....	0.179	0.192
In the Humates :		
Lime, $\text{CaO}$ .....	0.892	1.030
Potash, $\text{K}_2\text{O}$ .....	0.075	0.089
Nitrogen .....	0.041	0.094

The amount of humus originally in the soil was exceptionally low for a North Dakota soil, but by continuous cropping it has been reduced thirty-nine per cent., while the nitrogen of the humus has been reduced fifty-six per cent., leaving so small an amount of humus and of nitrogen in the humates that it is ques-

tionable whether the soil would supply proper food for the growing crop. We find similar conditions, but to a less marked degree in the other mineral constituents of the soil. This investigation of the humus, even with our lack of knowledge of the true nature of humus and humates, throws great light upon the character of the soil and the possible cause for a declining crop.

#### RELATION OF MINERAL MATTER TO HUMUS.

Does the mineral matter of the humates change with the decrease and increase of humus in the soil? The soil that we have just examined answers in part this question, but examinations made with the soils from the college farm showed in 1891 that the average humus content for the fields that had produced wheat for fifteen years was 126,000 pounds per acre, taken to a depth of one foot, while for surrounding unbroken prairie the average gave 218,000 pounds per acre, a loss by continuous cropping, burning of stubbles, etc., of 92,000 pounds, or of 42.2 per cent.

In another case where both the humus and phosphoric acid in the humates had been determined, we find :

	PER CENT.	
	Humus.	P <sub>2</sub> O <sub>5</sub> in humates.
1891 .....	5.35	0.079
1894 .....	6.82	0.091
1898 .....	7.86	0.117

For fifteen years previous to 1891 it is said the field had been cropped continuously to wheat. Beginning with 1892 a system of crop rotation has been followed, and the productivity of the field has continued to increase.

An acre of this soil then to the depth of one foot contained of humus and of phosphoric acid, P<sub>2</sub>O<sub>5</sub>, in the humates :

	Humus. Pounds.	P <sub>2</sub> O <sub>5</sub> in humates. Pounds.
1891 .....	119,037	1,758
1894 .....	151,745	2,025
1898 .....	174,885	2,603

The gain in humus from 1891 to 1898 has been 46.9 per cent., while the gain of phosphoric acid in the form of humates

has been forty-eight per cent. It will be observed that the gain in phosphoric acid in the humates has been expressed as per cent. almost the same as the gains for the humus in the same period. It has also been shown by Snyder<sup>1</sup> that when prepared humus is added to soils it combined with the mineral matter of the soil, forming humates.

If we calculate the nitrogen to show per cent. in humus, and the other mineral constituents to per cent. in humates, we shall have other relations brought out in a way not shown by the previous tables.

TABLE SHOWING PER CENTS.

Number.	Nitrogen in humus.	In humates.		
		Phosphoric acid, $P_2O_5$ .	Lime, CaO.	Potash, $K_2O$ .
411	4.43	1.26	4.03	1.62
413	4.33	1.82	2.85	4.48
414	5.93	1.63	3.74	1.48
415	3.55	...	...	...
416	3.98	2.09	7.82	1.01
417	4.87	2.14	8.32	2.51
419	1.41	2.17	2.14	1.90
420	1.07	4.66	25.57	1.98
421	2.20	4.49	24.12	2.08
422	1.91	3.43	17.44	...
423	2.26	0.87	2.42	1.36
424	2.13	1.26	2.94	1.37
425	2.22	0.96	2.31	1.35
426	2.23	0.83	3.35	1.40
427	1.90	0.92	3.01	1.60
428	2.65	1.08	2.65	1.20
270a	3.30	1.48	0	....
270b	6.01	1.87	5.79	....
86a	4.02	1.56	2.74	....
86b	3.68	1.80	2.90	....
277a	4.42	0.94	1.81	....
277b	7.40	trace	5.39	....
81a	4.00	1.54	5.71	....
81b	3.03	2.05	5.07	....

Other experiments are now in progress to answer some of the many questions that have been suggested by the foregoing.

AGRICULTURAL COLLEGE, N. D., September 20, 1898.

<sup>1</sup> This Journal, 19, 738.

## THE LE SUEUR PROCESS FOR THE ELECTROLYTIC PRODUCTION OF SODIUM HYDROXIDE AND CHLORINE.<sup>1</sup>

BY CHARLES LATHROP PARSONS.

Received September 17, 1898.

### HISTORY.

ERNEST A. LE SUEUR enjoys the distinction of having invented the first electrolytic process for the commercial decomposition of sodium chloride, which became a regular contributor to the markets of the world. Since February, 1893, caustic soda and bleaching powder have been manufactured at Rumford Falls, Maine, on a commercial scale. Le Sueur is now general manager of the plant, and deserves the highest credit for his efforts in this important branch of chemical science and industry.

He first began his experiments in the winter of 1887-88, and after associating with him Charles N. Waite, who afforded him valuable assistance and some facilities at his chemical works at Newton, Mass., they together ran an experimental cell from October, 1890, to May, 1891, in a paper mill at Bellows Falls, Vermont. In the meantime, Le Sueur had applied for his patents, and having obtained a cell giving an efficiency of rising seventy per cent., he went to England in May, 1891, for the purpose of presenting his process at the seat of the alkali industry. There he met with much encouragement from scientific men, but with discouragement so far as the adoption of his method on a commercial scale was concerned. The article of Cross and Bevan<sup>2</sup> gives a good description of the method at the time, but as theirs is the only authoritative article ever published regarding the process, it is not at all strange that Lunge<sup>3</sup> has some doubts of a method which must renew its diaphragms every forty-eight hours, and which converts its caustic solution into bicarbonate. As a matter of fact, carbonate of soda, as sodium carbonate or acid carbonate, has never been a product and the diaphragms are renewed so seldom that their cost is a mere incident of the process.

<sup>1</sup> Read at the Boston meeting of the American Chemical Society, August, 1898.

<sup>2</sup> *J. Soc. Chem. Ind.*, December, 1892.

<sup>3</sup> *Alkali Industry*, Vol. III.



In 1892, an association was formed, which in August of that year began the erection of a plant at Rumford Falls, and in February, 1893, began the manufacture of caustic soda and bleaching powder, using, to generate the required electricity, one 200 kilowatt dynamo of the Thompson-Houston pattern. The success of the venture was such that three more dynamos of the same capacity were installed in the fall of 1894, and the Electro-Chemical Company was organized. As a member of that company since its inception, I am fortunate in having the cooperation of Mr. Le Sueur and in being authorized to present to you a description of the process as it is running to-day, with such comments on past experience as I may deem of interest to you.

#### THE PROCESS.

The first practical working cell devised and used is well illustrated in the accompanying figure (Fig. 1), and is much the

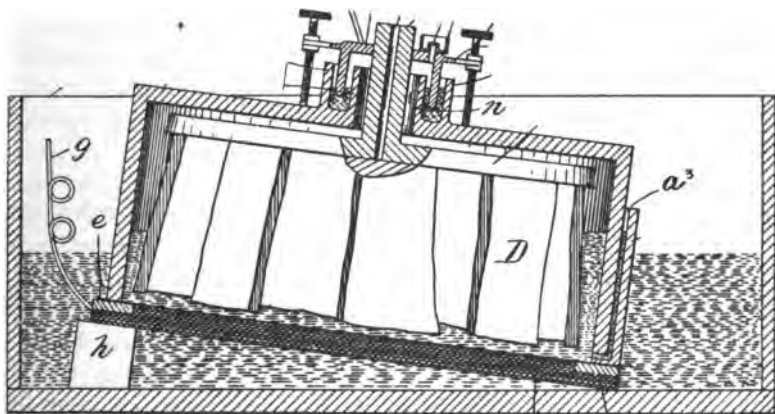


FIG. 1.

same as that described by Cross and Bevan in their aforementioned article. It consisted essentially of a bell of earthenware containing the gas carbon anode, and having its mouth covered by the diaphragm which was in contact with the anode, and was held in place by iron wire gauze forming the cathode of the cell. The whole was placed in an iron tank containing saturated brine and the bell was filled with brine to a level above that of the cathode compartment. The electrodes were close together,

and the internal resistance of the cell was small. The carbon anode was produced from large pieces of gas carbon imbedded in lead at one end above the liquid, and usually packed with smaller pieces of carbon, so as to give a large anode surface in contact with the diaphragm (see Figs. 2, 3, and 4). The iron



FIG. 2.

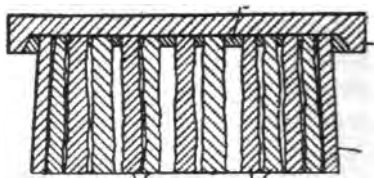


FIG. 3.

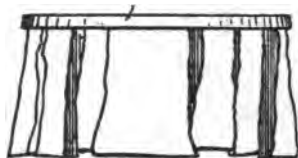


FIG. 4.

wire gauze forming the cathode was never in contact with the chlorine gas, and was so little acted upon by the caustic soda solution that it was one of the most permanent parts of the cell. This is also true of the iron tanks containing the cells and caustic solution. The diaphragm consisted of asbestos and had to be renewed every few weeks. This diaphragm was by no means expected to entirely prevent all diffusion of sodium hydroxide into the anode compartment nor of some hypochlorite in the reverse direction, but it did largely prevent the two solutions from mixing. Such a cell gave a working efficiency of about seventy per cent. and could be worked with an electromotive force of about four volts. It was soon found that the earthenware bell was not a practical form of apparatus, as they were easily broken, and even cracked by change of temperature. Consequently a new form of covering was devised, made from slate, with a spruce frame, which came in contact with the

caustic solution only, and was little effected thereby. The essential features of the process remain the same.

On passing the current reactions took place much as described by Oettel,<sup>1</sup> the main one being the electrolysis of sodium chloride, forming sodium and chlorine, the sodium immediately attacking the water in the cathode compartment, giving off hydrogen and leaving sodium hydroxide in solution. The chief difficulty of the process has always been to keep the sodium hydroxide in its proper compartment, for with the very best of diaphragms a limited amount of diffusion into the anode compartment will take place. Secondary reactions at once set in between any diffused sodium hydroxide and the chlorine present, forming sodium hypochlorite, which in turn will partially diffuse into the outer space and, contrary to Oettel's experience, is not reduced at the cathode, but is oxidized to sodium chlorate either before diffusion or during the evaporation of the cathode solution, and is eventually recovered as a by-product in the form of potassium chlorate. Besides the formation of hypochlorite, the diffusing sodium hydroxide is itself partially electrolyzed and the oxygen produced will immediately attack the carbon of the anode, very much complicating matters by forming carbon dioxide. The electrolysis of sodium hypochlorite will also give rise to nascent oxygen and increase the amount of carbon dioxide produced. This formation of carbon dioxide is a very serious matter in the production of bleaching powder, for unless removed from the chlorine gas it renders impossible the manufacture of a standard grade. The carbon anodes may be graphitized, rendering them much more resistant, but this difficulty is entirely eradicated when platinum is used. All of the reactions taking place in the anode compartment have been, without reference to the diaphragm, largely reduced by two patents of Le Sueur, which have broadly protected features that are, in my opinion, essential to the successful production of sodium hydroxide and chlorine by any method electrolyzing salt solution and using a diaphragm. The first of these is to have the liquid of the anode compartment at a higher level than that of the cathode, thus diminishing the entrance of sodium hydroxide by diffusion; and the second is to add hydrochloric acid to

<sup>1</sup> *Chem. Ztg.*, 1894, pp. 18 and 69.

the anode compartment so as to keep the solution slightly acid. This hydrochloric acid so added at once decomposes any hypochlorite, and is itself oxidized so that all of its chlorine is regained in the form of that gas. No chlorine is lost by this operation, for the chlorine obtained as bleaching powder is just so much greater than the equivalent of the sodium hydroxide as the amount of chlorine in the hydrochloric acid added. To the Electro Chemical Company this use of hydrochloric acid is a matter of some expense, for an equivalent of chlorine at Rumford Falls costs a little more in the form of hydrochloric acid than it is worth in bleaching powder. It will readily be seen, however, that in other localities and, especially near Le Blanc soda factories, the use of hydrochloric acid would be a positive advantage from a standpoint of economy.

The Le Sueur cell at present in operation at Rumford Falls embodies all the essential features which I have outlined, but it is larger, simpler of construction, and the carbon anode has at last been discarded in favor of a special form of platinum anode recently invented by Le Sueur. The cell as now used (Fig. 5)

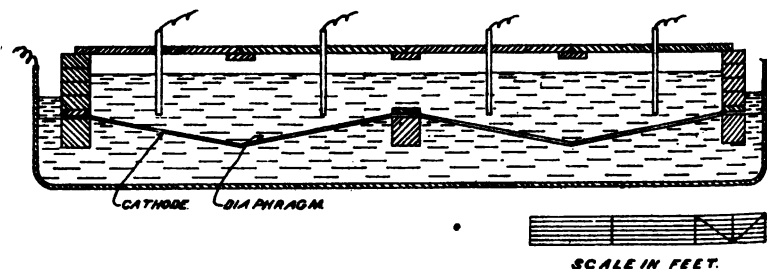


FIG. 5.

is contained in a tank five by nine feet and one and one-half feet deep, and made of one-quarter inch boiler steel. Excepting the asbestos, which composes the diaphragm, the wire netting of the cathode, and the materials of the positive electrode, it is built entirely of spruce, red brick, Portland cement, sand, and slate. These substances are so disposed in the cell as to be practically permanent, the wood being exposed to no action except that of the caustic solution, which has little effect upon it. The anodes are introduced from the top of the cell and may be removed singly without interrupting the process. Troublesome

joints are closed with a specially prepared plastic cement. The diaphragm is tipped somewhat from the horizontal for the purpose of permitting the easy egress of the hydrogen bubbles. The foundation of the cell within the tank consists of an oblong frame of spruce, eight feet four inches by four feet ten inches, outside measurement, and eight inches less on both dimensions inside. This frame is eleven inches deep, only the side pieces, however, resting upon the floor of the tank. The end pieces consist of four four-inch timbers whose upper surfaces are ten inches above the floor of the tank and one inch below the top surface of the longer side. The frame is divided transversely by a timber, similar to each of the end timbers, which crosses the middle of the frame at the same level as the end pieces. This center beam forms a bridge over which the flat iron ribs supporting the cathode are hung. The cell is thus divided into two equal spaces merely for mechanical convenience. The ribs referred to consist of four parallel pieces of flat iron, three of them being one and one-half by three-eighths inch, and the fourth, twice as wide. This wider piece is fastened at both ends to the containing tank, so as to receive from the latter the electric current which enters through the material of the tank and communicates the current to the cathode which rests upon these iron ribs. The diaphragm rests directly upon the cathode. The depth of the trough formed by the slanting ribs is four inches. There is an adequate arrangement at the ends of the bridge pieces by means of which the hydrogen, finding its way to this higher level, is delivered to exit pipes communicating with the atmosphere or with any system of piping to which it is desired to deliver it. The inch of space between the tops of the cross timbers and the side pieces is utilized to take a piece of slate four feet long by four inches wide by one inch thick. This presses down upon the diaphragm and the cathode netting and keeps all solid. On top of the sides and ends of the frame there are four courses of common brick laid in clear cement. There is a coating of cement applied to the inside walls of the portion of the cell forming the anode compartment, and this includes not only the brick walls, but the small portion of the wooden sides above the cathode which would otherwise come in contact with the anode liquid. The ceiling of the cell consists simply of pieces of slate

two feet by one foot, and suitably supported by transverse strips of slate one inch thick by four inches wide. Through the ceiling plates pass the glass tubes to which the anodes are attached.

The anodes which are now used are made from an alloy of iridium and platinum, and are so constructed that a very large anode surface is presented at an almost incredibly small cost when it is considered that it is not at all of the nature of a plated surface, but is an anode of solid metal. Sixty anodes on an average are used to each cell, and each anode costs seventy-three cents at the present market price of platinum. They are acted upon chemically but slightly if at all. If the glass holders break there is no loss of platinum and a new anode can immediately be put in place. The total cost for the anodes of a plant producing, per month, 200 tons of bleaching powder, is approximately \$5,000, or \$40 for a cell producing fifty-five pounds of sodium hydroxide and fifty pounds of chlorine per day; and this allows for a very low cell efficiency. The total cost for the renewal of the platinum, including labor, is less than half the cost of the bare carbon alone as it was formerly used. Besides, it must be remembered that carbon anodes are certain to give more or less carbon dioxide if hypochlorite be present, while with these iridio-platinum anodes no carbon dioxide can possibly be produced.

At Rumford Falls, the Electro-Chemical Company obtains power at a very low cost, so that it pays to obtain a maximum of work from each cell by using a higher current density in proportion to the anode surface than might be tenable under other conditions. As the cells are now constructed, a current of 1,000 amperes is passed through each cell under a pressure of six and one-half volts. I am aware that this voltage is high, and from a statement in Lunge,<sup>1</sup> he would probably, at first thought, condemn the process on this ground alone. But it will readily be understood how this increased voltage can be economically employed when it is considered that at \$8.00 per electrical horse power per year, which is the cost of power to the company at Rumford Falls, the extra cost per pound of product, on an average efficiency of eighty per cent., is but \$0.00015 for each extra volt used. This high voltage is, by no means, an essential of the

<sup>1</sup> Alkali Industry, Vol. III.

process, and each cell can be run on a lower amperage when, of course, less pressure would be required. It is simply a fact that, at Rumford Falls, it is economical to run the cells on this voltage, forcing through them all the current they can take without undue heating. Under these conditions, the renewal of the cell is usually made necessary only on account of the deterioration of the diaphragm. The diaphragms have an average life of seven weeks, and have been used twenty-four consecutive weeks without renewal. The cathodes are but little acted upon, and the steel tanks are practically indestructible.

The cells are arranged so that twenty-two are in series, and three series are run in parallel on two dynamos. The hydrogen is used only for working platinum, the larger part being allowed to escape into the atmosphere. The chlorine is conducted by earthenware pipes to lead chambers and absorbed by lime in the usual manner, although, at present, a part is used for the manufacture of potassium chlorate. The caustic solution is concentrated by evaporation *in vacuo* and is separated from the major part of the undecomposed salt by centrifugals. Any chlorate is now readily removed, and the solution is then boiled down in cast-iron kettles to a first quality caustic soda analyzing about seventy-four per cent. sodium oxide. The recovered salt is converted into brine and is used in the cathode compartment of the cells,—nothing but fresh brine and some hydrochloric acid being ever added to the anode side. Whole bays of twenty-two cells have shown daily averages of over ninety per cent. chlorine efficiency, and weekly averages of eighty-seven per cent. If the anode compartment could be kept constantly acid, as can be done with single cells, a chlorine efficiency approaching very closely to the theoretical may be reached. The efficiency reckoned upon the sodium hydroxide produced is not quite so high.

One great field for electrolytic processes is the production of bleaching liquors and caustic solutions for bleacheries, paper mills, and the like. Large economies might be introduced by companies of this kind by making their own solutions electrolytically instead of by the usual method of first transporting the chlorine in the form of bleaching powder and the alkali in the solid state. This is almost self evident when one considers that

the final evaporation of the caustic soda, which is quite costly, is done solely for purposes of transportation; that the absorption of chlorine by milk of lime is a very simple operation, and the bleach liquors, so produced, are much more efficient per unit of chlorine than bleaching powder; and that the raw material, salt, is easily and cheaply obtained and transported without deterioration, while a small plant can be run almost as economically as a large one. In fact, the Electro-Chemical Company has sold a great deal of chlorine in the form of bleach liquors to pulp mills, at reasonable distances from the works, that preferred to take this liquid carrier of chlorine on account of its ready settled solution, ease of manipulation, and its greater efficiency, although the cost of transportation might be somewhat greater. In works which do not require caustic soda the process would also be highly economical for under such conditions the cathode liquor can be directly used to absorb the chlorine, in excellent condition for bleaching purposes, thus doing away entirely with the cost and use of lime. I do not hesitate to predict that we shall yet see many Le Sueur plants established in connection with mills now using bleaching powder. In fact one of our largest American sulphite pulp mills has already made arrangements for a trial of the Le Sueur plant with the view of bleaching to a very large extent.

In closing, allow me to call your attention to the fact that any process for the production of caustic soda and bleaching powder has had to struggle under great difficulties during the last six years on account of the tremendous fall in the market price of those commodities, and without great inherent merit no electrolytic process could have survived its infancy. This fall in price has been due to the vigorous competition of the alkali industries of England and of Germany, and of increased home production, rather than from any improvement of old methods, or from the establishment of new processes. The fact that both England and Germany have a freer market in this country to-day than they had when the first electrolytic process was introduced, is also, in part, responsible for the fall in price. In 1892, when the plant at Rumford Falls was built, bleaching powder sold in Boston for \$45.00 per ton, and caustic soda for \$74.00



per ton. The prices to-day are \$30.00 and \$36.00 respectively. The fall in price of products here shown is equivalent to eighty per cent. of the present total gross income, and means that any surviving process must have reduced, not only its operating expenses, but also its profits. It is not at all surprising that under such adverse conditions many electrolytic methods have failed commercially.

The question of cost of production is one of prime interest to the alkali manufacturer, but depends very largely upon location, and upon cost of power. In the following estimate prices are given which are liberal for Western New York, where cheap power may be obtained. Salt, in the form of brine, and lime might be procured in other places much cheaper, and allowance is made for a much larger amount of hydrochloric acid than is now used. Where power is provided in the form of electricity, as at Niagara Falls, there is no cost for power installation.

Cost of plant for producing 20,000 pounds prime bleaching powder and 7,000 pounds caustic soda per day would be, exclusive of power and generator installation, \$60,000.

## DAILY OUTLAY.

Salt, 13,000 pounds (at \$2.50 per ton laid down)	\$16.25
Lime, 10,000 pounds (at \$5.00 per ton laid down)	25.00
Muriatic acid (2,000 pounds hydrochloric acid)	20.00
Coal (for evaporating, and incidentally generating 250 H. P. of the total power required), seven gross tons at \$3.00 .....	21.00
Labor, forty-five men, at average of \$1.60 .....	72.00
Superintendence and bookkeeping .....	7.50
Packages .....	15.00
Oil, waste, and sundries .....	10.00
Taxes and insurance .....	5.00
Repairs and sinking fund .....	25.00
Miscellaneous .....	5.00
Power, 1,000 H. P. (at \$12.00 per E. H. P. year) .....	33.00

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Total daily cost..... \$254.75

## DAILY OUTPUT.

20,000 pounds bleaching powder, at 1½ cents...	\$300.00
7,000 pounds caustic soda, at 1½ cents.....	105.00
	<hr/>
	405.00
Less freight to market and commission.....	55.00
	<hr/>
Total daily income.....	\$360.00

Local conditions effecting cost of raw material, freight, and power, and changes in market price of product, would greatly influence the value of this estimate. With these figures, however, any one may readily calculate the probable cost in any locality when the conditions affecting it are known.

NEW HAMPSHIRE COLLEGE,  
DURHAM, N. H.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE CASE SCHOOL  
OF APPLIED SCIENCE.]

## COMPOSITION OF OHIO WINES.

BY ALBERT W. SMITH AND NORMAN PARKS.

Received September 2, 1898.

NORTHERN Ohio is one of the most important grape-growing regions in the United States, and produces no inconsiderable quantity of wine from the yearly growth, but, so far as we are aware, no systematic study of the chemical composition of these wines has ever been undertaken. In order to determine whether a sample of wine is pure or not, it is often necessary to know what is the average chemical composition of samples of guaranteed purity, made from the same kind of fruit and grown in the same region. An examination of a large number of Ohio wines, bought in this market, showed a considerable variation in composition from the average of French, German, and California wines. It was thought desirable to ascertain if this was due to a very universal sophistication of Ohio-made wines in this market, or whether it was due to an actual difference in the nature of the fruit grown here, or possibly in the method of manufacture and fermentation.

In the fall of 1894, and of 1895, samples of most of the prominent varieties of Ohio grapes were collected, the juice expressed

and converted into wine according to the manner generally practiced in this locality. Both seasons were favorable to the growth of fine fruit, and, as nearly as possible, an average quality of each sample was selected. In every case the fruit was mature and fully ripened when gathered. No fermentation was allowed to take place between the times of grinding and the pressing of the juice from pulp and stems.

Fermentation was carried on in jugs, at the temperature of the outside air, until freezing weather, when the jugs were placed in a cool cellar until February. The wine was then carefully siphoned into bottles and further fermentation arrested by Pasteurizing at 160° F. The bottles were then corked and stored until wanted for analysis. In all cases except two, the samples were about one year old when analyzed. The samples made from Concord and Catawba grapes were two years old. The methods of analysis used were those published in Bulletin 43, U. S. Department of Agriculture, Division of Chemistry.

The results are expressed in Table I as grams per 100 grams of wine, or per cent. by weight. In Table II are the results of analyses of a number of typical samples of wine sold in the markets of Northern Ohio.

Comparing the results of analyses of these twelve samples of pure wines with those of European origin, made from similar fruit,<sup>1</sup> it is noticeable that gravity, acidity, and proportion of alcohol, potassium acid tartrate, and tartaric acid are quite similar. The average of solids in the Ohio samples is slightly lower than that of the foreign-grown wines. These latter contain usually somewhat more than two per cent., though individual cases occur which fall below this limit.

The most important differences are in the percentages of glycerol and ash. Published reports of European samples indicate the ash usually above two-tenths per cent. and from five-tenths to eight-tenths per cent. glycerol, while the maximum and minimum for those analyzed here are 0.15 and 0.10 for ash, and 0.95 and 0.29 per cent. respectively, for glycerol.

Since these two constituents, together with the solids, are of most importance and general use in determining the genuine-

<sup>1</sup> Fresenius : *Ztschr. anal. Chem.*, 36, 413.

TABLE I.

Variety of grapes.	Grams per 100 grams wine.											
	Concord.	Ives.	Hayse.	Catawba No. 1.	Centennial.	Warden.	Hartford.	Delaware.	Riesling.	Niagara.	Catawba No. 2.	Catawba No. 3.
Specific gravity . . . . .	0.9921	0.9971	0.9959	1.0010	0.9934	0.9970	0.9977	0.9909	1.0060	0.9931	0.9918	0.9972
Total acid as acetate . . . . .	0.27	0.29	0.23	0.32	0.30	0.36	0.91	0.30	1.46	0.26	0.26	0.37
Alcohol . . . . .	12.0	8.45	7.90	10.5	8.20	7.40	5.10	11.5	3.30	8.77	11.4	8.82
Glycerol . . . . .	0.55	0.42	0.36	0.51	0.40	0.42	0.29	0.45	0.39	0.50	0.50	0.95
Solids . . . . .	1.93	1.61	1.51	3.66	1.28	1.81	1.55	1.65	2.29	1.58	2.00	3.86
Ash . . . . .	0.14	0.14	0.14	0.15	0.11	0.13	0.15	0.12	0.12	0.10	0.12	0.12
Phosphoric anhydride . . . . .	0.004	0.005	0.008	0.003	0.001	0.009	0.003	0.005	0.004	0.007	0.005	0.008
Sugar . . . . .	0.11	0.12	0.11	1.54	0.11	0.92	0.12	0.10	0.10	0.11	0.07	...
Nitrogen . . . . .	0.007	0.009	0.008	0.007	0.005	0.011	0.005	0.017	0.008	0.008	0.013	...
Volatile acid as acetic . . . . .	...	...	...	0.031	0.20	0.11	0.12	0.07	...	0.12	0.21	0.30
Potassium bitartrate . . . . .	0.31	0.28	0.40	0.30	0.23	0.24	0.31	0.24	0.20	0.16	0.25	0.20
Free tartaric acid . . . . .	0.05	0.10	0.12	0.11	0.08	0.09	0.10	0.08	0.07	0.05	0.03	0.05
Tannin . . . . .	0.04	...	...	0.04	0.02	0.03	0.03	0.03	0.02	0.02	0.02	0.03
Glycerol as parts per 100 parts alcohol . . . . .	4.5	4.8	4.6	4.9	4.8	5.7	5.7	3.9	11.8	5.6	4.4	10.7

TABLE II.

Grams per 100 grams wine.

Kind.	Solids.	Alcohol.	Ash.	Acid as tartaric.	Glycerol.	Reducing sugar.	Sucrose.	Volatile acid as acetic.
Sour Catawba.....	1.42	8.19	0.20	0.45	0.57	0.15	none	0.30
" " .....	1.42	11.95	0.16	0.22	0.51	0.18	none	0.45
" " .....	1.54	9.86	0.15	0.27	0.57	0.14	none	0.20
" " .....	1.59	15.65	0.09	0.45	0.45	0.26	none	0.32
" " .....	1.45	10.24	0.24	0.30	0.38	0.20	none	0.20
" " .....	2.26	10.57	0.14	0.27	0.37	0.28	none	0.30
" " .....	1.75	9.24	0.10	0.20	0.27	0.25	none	0.17
" " .....	1.36	10.45	0.13	0.48	0.48	0.30	none	0.33
Sweet Catawba....	13.7	20.20	0.40	0.38	0.33	13.00	none	0.31
" " ....	14.0	13.80	0.27	0.23	0.46	12.7	none	0.19
" " ....	16.9	12.10	0.15	...	...	16.4	none	0.20
" " ....	15.9	9.80	0.15	...	...	14.2	none	...
" " ....	18.9	9.07	0.17	...	0.17	14.5	0.90	...
" " ....	15.0	9.92	0.21	...	0.24	13.6	none	...
Port Wine.....	14.8	19.3	0.20	0.15	0.28	14.7	none	...
" " .....	20.3	8.92	0.19	...	0.49	15.4	1.47	...
" " .....	10.8	18.7	0.24	...	0.31	9.1	none	...
California Port ...	11.6	16.7	0.30	...	0.39	13.2	none	...
" " ...	13.11	16.9	0.25	0.30	0.30	...	none	...
Old Angelica.....	15.1	17.3	...	0.25	0.31	14.2	none	...
Sherry .....	4.71	13.8	0.31	...	0.45	3.1	none	...
Niersteiner .....	1.57	9.29	0.22	0.30	0.97	...	none	...
Muscatel .....	16.2	17.2	0.22	0.08	0.09	...	none	...
" .....	15.1	20.7	0.21	0.20	0.33	13.2	none	...

ness and purity of a sample of wine, these differences are most important. Most authorities state that, in the natural process of alcoholic fermentation, glycerol and alcohol are produced in the ratio of from 7 to 14 parts of the former to 100 parts of the latter. If this be always true, the inference to be drawn, when this maximum is exceeded, is that glycerol has been added, while in case the ratio of glycerol to alcohol is below 7 : 100, that the sample has been fortified by the addition of alcohol foreign to the product of fermentation. Such conclusions in the case of these Ohio wines would be quite misleading. In the same manner, care must be exercised, when these wines are under considera-

tion, in drawing conclusions as to the addition of water, from the facts of low ash and solids.

The skilful adulteration of wine is extremely difficult to detect by chemical analyses, and these abnormally low results, obtained by analysis of perfectly pure and reliable samples, make such conclusions from these determinations all the more unsatisfactory.

It is of interest also to compare the composition of these samples with that of authentically pure California samples. Many such analyses have been made and reported by Prof. Hilgard,<sup>1</sup> and while they do not include determinations of glycerol, the contents of ash and solids are usually higher than those of European samples.

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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 3.]

### THE DETERMINATION OF SULPHUR IN ASPHALT.

By E. H. HODGSON.

Received September 22, 1898.

THE numerous articles recently published on the analysis and chemistry of asphalts, and the wide range of opinion as to the relative values of the different methods in use for the determination of sulphur, have led me to make a comparison of results on some typical asphalts.

Dr. E. H. Miller, through the kindness of Mr. A. W. Dow, of Washington, was enabled to secure samples, the sources and natures of which were known. The samples were labeled Trinidad Lake, Trinidad Crude, Trinidad Lake Refined, Cuban Crude, Alcatraz Crude, and California Crude, and were described by Mr. Dow as follows:

*Trinidad Lake.*—Asphalt from the lake on the island of Trinidad, imported by Barber Asphalt Co. for paving.

*Trinidad Crude.*—Crude asphalt from Hadley's Diggings, about one mile from Trinidad Lake. It is known as "iron pitch," being the hardest asphalt found in Trinidad.

*Trinidad Lake Refined.* This is crude Trinidad Lake asphalt, melted up to drive out the water.

*Alcatraz Crude.*—From Ventura Co., California, used by

<sup>1</sup> Bulletin 13, Division of Chemistry, U. S. Department of Agriculture.

the Alcatraz Asphalt Co. for paving, after the addition of liquid asphalt.

*California Crude.*—From Kern Co., California, used by the Standard California Asphalt Co. for paving, after the addition of liquid asphalt.

Sample "Trinidad Lake" was found to lose water very rapidly, so it was heated to about 60° C. (not sufficient to melt it) and then remained constant.

The samples were ground as fine as possible in a mortar, and then placed in glass bottles, fitted with tight corks. From these bottles average samples were taken and kept in test-tubes for use.

HEATING WITH STRONG NITRIC ACID IN A SEALED TUBE—  
CARIUS' METHOD.

The tubes were made in the usual way from heavy glass tubing. Two determinations were made on each sample. One on one-half gram and one on three-fourths gram. A general description of the method is as follows: One-half gram of asphalt is introduced into the bottom of the tube, and fifteen cc. of fuming nitric acid (1.60 sp. gr.) is poured upon it. The open end of the tube is then drawn out into a thick-walled fine-caliber tube, but not sealed. The tube is then heated, for about six hours, in a water-bath kept at 80°–90° C. Then five cc. more acid are added, the tube is sealed, and heated in a guarded furnace at a temperature of about 150° C. for from four to five hours. Allow the tube to cool, then open and reseal, and reheat for from two to four hours at a temperature of 180°–200° C. Cool, open, and remove the liquid and residue into a No. 2 beaker. Dilute with water, filter, and wash. If the residue contains anything but sand it is saved and treated separately. The filtrate is evaporated to dryness on the water-bath, adding a piece of solid sodium hydroxide. The nitric acid is driven out by repeated evaporation of the solution, with the addition of hydrochloric acid, and the silica dehydrated in an air-bath at 110°–115° C. Cool the dehydrated mass, add two to three cc. of hydrochloric acid and 100 cc. of water, stir well, filter, and wash well with hot water. Dilute the filtrate to about 200 cc., heat to boiling and while boiling add twenty cc. of barium chloride (twenty per cent. solution), drop by drop, from a burette, at the rate of

about a drop a second. Stir all the time. Boil the solution about ten minutes, and allow it to stand twenty-four hours. Filter, wash with hot water, and ignite. Treat with sulphuric acid and reignite. Then cool and weigh the barium sulphate. A pure white product was obtained, and the precipitate did not run through the filter.

*The residue* from the sealed tube, if not thoroughly oxidized, is fused with six grams of mixed carbonates and one gram of potassium nitrate. The fusion is dissolved in water and hydrochloric acid. The nitrates are destroyed by evaporating with the addition of hydrochloric acid, and the silica dehydrated as before. Filter off the silica and wash. Then determine the sulphuric acid in the filtrate as before described.

When three-fourths gram of asphalt was used, twenty-five cc. of fuming nitric acid were employed instead of twenty cc.

The following results were obtained :

#### TRINIDAD LAKE.

	Weight of barium sulphate. Gram.	Sulphur. Per cent.
One-half gram .....	0.1526	4.192
Residue .....	0.0051	0.140
		<hr/> 4.332
Three-fourths gram .....	0.2238	4.10
Residue .....	0.0068	0.18
		<hr/> 4.28

#### TRINIDAD CRUDE.

One-half gram .....	0.1249	3.400
Residue .....	0.0034	0.086
		<hr/> 3.486
Three-fourths gram .....	0.1720	3.148
Residue .....	0.0106	0.19
		<hr/> 3.338

#### TRINIDAD LAKE REFINED.

One-half gram .....	0.1585	4.35
Residue .....	....	....
		<hr/> 4.35



	Weight of barium sulphate. Gram.	Sulphur. Per cent.
Three-fourths gram.....	0.2160	4.21
Residue .....	0.0137	0.25
		4.46
CUBAN CRUDE.		
One-half gram.....	0.1315	3.61
Residue .....		....
		3.61
Three-fourths gram.....	No results.	
ALCATRAZ CRUDE.		
One-half gram.....	0.1839	5.05
Residue .....	0.0195	0.54
		5.59
Three-fourths gram.....	0.2749	5.12
Residue .....	0.0294	0.46
		5.58
CALIFORNIA CRUDE.		
One-half gram .....	0.2589	7.11
Residue .....	0.0145	0.398
Three-fourths gram.....	No results.	

## DEFLAGRATION METHOD—S. F. AND H. E. PECKHAM.

A porcelain crucible is heated to a dull red heat, and *small* amounts of a mixture of one gram finely ground asphalt, eight grams of potassium nitrate, and eight grams of mixed sodium and potassium carbonates, added from time to time, just keeping the material in the crucible melted. When all of the mixture has been added, heat to perfect fusion with a blast-lamp, and cool. Dissolve the fusion in twenty cc. hydrochloric acid and forty cc. of water, and wash the crucible well with hot water. The solution is evaporated down to dryness, dehydrated at  $110^{\circ}$ – $115^{\circ}$ , the silica filtered off, and the sulphuric acid determined in the filtrate as before. The results are as follows:

TRINIDAD LAKE.		
No.	Weight of barium sulphate. Gram.	Sulphur. Per cent.
1 .....	0.2770	3.804
2 .....	0.2689	3.68

## TRINIDAD CRUDE.

No.	Weight of barium sulphate. Gram.	Sulphur. Per cent.
1 .....	0.2443	3.37
2 .....	0.2359	3.24

## TRINIDAD LAKE REFINED.

1 .....	0.2634	3.62
2 .....	.....	....

## CUBAN CRUDE.

1 .....	0.2009	2.76
2 .....	0.2052	2.82

## ALCATRAZ CRUDE.

1 .....	0.3054	4.19
2 .....	0.2773	3.81

## CALIFORNIA CRUDE.

1 .....	0.4376	6.50
2 .....	.....	....

## SODIUM PEROXIDE METHOD.

Place one gram of the fine asphalt in the bottom of a large nickel crucible. Cover with a layer of about four grams of mixed carbonates and about one gram of solid sodium hydroxide. Cover the crucible and heat gently until the gases are driven off. Then raise the heat and add small amounts of sodium peroxide, from time to time, until no further action is noticed on the addition of fresh  $\text{Na}_2\text{O}_2$ . Then, with the blast-lamp, heat to perfect fusion. This takes but a few minutes. Pour as much of the fusion as possible upon the cover of the crucible and cool slowly. Place the fusion, crucible, and cover in a casserole containing fifty cc. hot water, and after thorough digestion on the water-bath, filter off the residue, and wash well with hot water. The filtrate is made acid with hydrochloric acid, and evaporated down to dryness, dehydrated at  $110^\circ$ – $115^\circ$  C., the silica filtered off, and the sulphuric acid determined in the filtrate as already described. Results by this method:

## TRINIDAD LAKE.

No.	Weight of barium sulphate. Gram.	Sulphur. Per cent.
1 .....	0.2687	3.69
2 .....	0.2744	3.77

## TRINIDAD CRUDE.

No.	Weight of barium sulphate. Gram.	Sulphur. Per cent.
1 .....	0.2426	3.33
2 .....	0.2360	3.25

## TRINIDAD LAKE REFINED.

1 .....	0.2962	4.07
2 .....	0.2929	4.02

## CUBAN CRUDE.

1 .....	0.2256	3.10
2 .....	0.2230	3.06

## ALCATRAZ CRUDE.

1 .....	0.2887	3.97
2 .....	0.2880	3.96

## CALIFORNIA CRUDE.

1 .....	0.4557	6.26
2 .....	0.4481	6.15

## IGNITION WITH CALCINED MAGNESIA—ESCHKA'S METHOD.

One gram of finely ground asphalt is intimately mixed with one gram of calcined magnesia and about one-half gram of dry mixed carbonates is added. Mix well and place in a platinum or porcelain crucible. With the crucible in an inclined position, heat at a dull red heat, stirring every few minutes until the ash is a dull yellow. Cool and add about one gram of finely ground ammonium nitrate and mix thoroughly. Heat slowly to a dull red, and continue the heating until the ammonium nitrate is entirely decomposed. Cool, extract the mass thoroughly with water (hot water preferred), filter, and wash well. Acidulate the filtrate with hydrochloric acid, and precipitate the sulphuric acid as before described. The results are as follows :

## TRINIDAD LAKE.

No.	Weight of barium sulphate. Gram.	Sulphur. Per cent.
1 .....	0.2660	3.65
2 .....	0.2791	3.83

## TRINIDAD CRUDE.

1 .....	0.2608	3.58
2 .....	0.2567	3.53

## SULPHUR IN ASPHALT.

## TRINIDAD LAKE REFINED.

No.	Weight of barium sulphate. Gram.	Sulphur. Per cent.
1 .....	0.2744	3.77
2 .....	0.2650	3.64

## CUBAN CRUDE.

1 .....	0.2020	2.77
2 .....	0.1941	2.66

## ALCATRAZ CRUDE.

1 .....	0.3054	4.19
2 .....	0.3021	4.16

## CALIFORNIA CRUDE.

1 .....	0.5011	6.88
2 .....	0.5109	7.01

The relative accuracy of the different methods is best shown by tabulating the results, as follows :

	Trinidad Lake. Crude.	Trinidad Lake Refined.	Cuban Crude.	Alcatraz Crude.	Califor- nia Crude.
Sealed tube.....	4.33	3.49	4.35	3.61	5.59
	4.28	3.34	4.46	...	5.57
Deflagration ....	3.80	3.37	3.62	2.82	4.19
	3.68	3.24	...	2.76	3.81
Peroxide.....	3.69	3.33	4.07	3.10	3.97
	3.77	3.25	4.02	3.06	3.96
Eschka's.....	3.65	3.58	3.77	2.77	4.19
	3.83	3.53	3.64	2.66	4.16

It would appear, therefore, that the "sealed tube" gives the most accurate results, but on account of the explosion of the tubes and the time required for a determination, it would probably be barred out.

The deflagration method apparently gives low results. It is much shorter than the sealed tube, but longer than either the peroxide or Eschka's method.

Of the latter two, the Eschka's method is perhaps the better, as it requires less time and attention to carry out, and gives about as good results.

The peroxide method is shorter than the deflagration method and about as accurate.

The reagents employed were first tested for sulphur.

	Sulphur. Per cent.
The sodium and potassium carbonate contained.....	0.005
The sodium peroxide contained.....	0.003

The rest of the reagents were sulphur free or contained but the merest trace.

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#### NOTE.

*Testing for a Yellow Azo-Color in Fats, Etc.*—In this Journal, 20, 110, Joseph F. Geissler describes a delicate test for the detection of a yellow azo-dye used in coloring fats. The test has proved of the greatest service to me, and I make use of it constantly. While experimenting upon the subject, I have noted another simple test for this azo-color that seems fully as delicate as Geissler's. To a few cubic centimeters of the pure filtered fat in a large test-tube are added an equal volume of a mixture of one part strong sulphuric acid, and four parts glacial acetic acid. The contents of the tube are then heated almost to boiling, and thoroughly mixed by violently agitating the bottom of the tube. When now allowed to stand and separate, the lower layer of mixed acids will be strongly colored wine-red if the azo-color be present. Pure butter-fat imparts no color, or at most only a very faint brownish tinge to the acids. Strong hydrochloric acid may replace the sulphuric in the above mixture, or a mixture of one part strong sulphuric acid, and three parts water may be used, but I have obtained the best results in the manner described.

ALBERT H. LOW.

DENVER, COLORADO, August 27, 1898.

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#### NEW BOOKS.

A BRIEF COURSE IN QUALITATIVE ANALYSIS. BY ERNEST A. CONGDON, PH.B., F.C.S. New York: Henry Holt & Co. 1898. iv + 62 pp. Price 60 cents.

Professor Congdon has given us a very satisfactory little text-book. While brief, the course, so far as it goes, is quite thorough.

The arrangement of the book is excellent and the selection of matter carefully made. Blank leaves for notes are inserted between the pages. The classification of the metals into groups for the purpose of analysis is first shown. Then the reactions of the metals are given. Following the single reactions of each group is given the method of analysis for the group. In most cases an alternative scheme is also printed. A notable exception is in the case of the barium group where the writer gives only the separation of strontium from barium, depending on the different solubilities of their nitrates in absolute alcohol. The reactions of the acids follow those of the metals. The order is alphabetical and not according to groups. The scheme for the detection of iodides, chlorides, and bromides, where more than one is present, by separate tests for each, does not commend itself to the reviewer, and might well be substituted by Professor Hart's easier and simpler method. The section on the treatment of solids is clearer and more concise than that given in most small books. Throughout the book the aim of the writer seems to have been to make the student think. This is borne out by the notes which follow the analytical schemes and by the table of solubilities and list of questions which close the book.

RICHARD K. MEADE.

**ALKALOIDAL ESTIMATION; A BIBLIOGRAPHICAL INDEX OF CHEMICAL RESEARCH PREPARED FROM ORIGINAL LITERATURE FOR THE COMMITTEE OF REVISION.** BY PAUL I. MURRELL, under the direction of ALBERT B. PRESCOTT. Ann Arbor, 1898. "Published by the Committee of Revision" of the Pharmacopoeia of the United States of America, 1890-1900. Not for sale.

This is a pamphlet of 58 pages "in boards," and embraces the easily found work upon its title subject from 1861 to 1898. It consists entirely of clerical labor very well done and its arrangement is convenient for reference.

The contents are first a list of the more important of the series of publications examined, and then an alphabetical list of other periodicals to which references are given. Then the body of the work is in three parts.

Part I is the chronological index where, in giving the references, original papers are first given. Then republications and abstracts; and the abbreviations used are, as far as practicable, those of Bolton's "Bibliography of Chemistry."

Part II is an alphabetical index of authors referred to with dates and reference numbers to the dates in Part I.

Part III is a subject index where a similar arrangement of dates and numbers are used, the subject coming first in alphabetical order, and the name of the author last.

On pages 10, 11, and 12, are given the full text of the assay processes of the British Pharmacopoeia of 1885 for cinchona, nux vomica, and opium, and on pages 38, 39, and 40, are given the full text of the assay processes of the same Pharmacopoeia of 1898 for belladonna, cinchona, ipecac, nux vomica and opium tincture.

On pages 33 and 34, are given a translation of the assay processes of the German Pharmacopoeia of 1895 for cinchona and opium, and on pages 22, 23, 24, 25, and 26, are given the assay processes of the U. S. Pharmacopoeia of 1890 for cinchona, nux vomica, and opium.

The recent British Pharmacopoeia gives also an assay process for opium which is not quoted here apparently because it is so nearly identical with the process for making the tincture of opium by assay. But it would have been better to have quoted the process for opium rather than that for the tincture, since it is very convenient to have all the complete pharmacopoeial processes quoted here together for ready reference in accordance with the general plan of the pamphlet.

The chief utility of this work outside of the Committee of Revision, is in the time and labor that may be saved by it to any one who is about to undertake any research or investigation of any of the natural alkaloids, and although its field is not large it is rather to be regretted that the "pamphlet is not for sale." It is however altogether probable that any one needing a copy may get it from the committee.

E. R. SQUIBB.

TRAITÉ D'ANALYSE DES SUBSTANCES MINÉRALES. PAR A. CARNOT.  
Tome premier.—Méthodes Générales d'Analyse Qualitative et Quantitative. Paris: V<sup>re</sup> Ch. Dunod, Editeur. 1898. 992 pp.

This treatise on mineral analysis by M. Carnot is to consist of three volumes of about 1000 pages each. The first volume which has just been issued comprises 992 pages of which 459 are devoted to qualitative methods.

The first chapter treats of the blowpipe and blowpipe methods including heating in open and closed tubes, on charcoal and on the end of a platinum wire; flame reactions and fusion in borax and microcosmic-salt beads; fusion with sodium carbonate, with reagents on charcoal and on platinum foil; the tests for sulphur and examination with cobalt solution. The separation and distinctive tests for the metals are given tersely and clearly.

Chapter 2 treats of the Bunsen burner, and contains a scheme for the systematic examination of a sample by the previously described methods.

Chapter 3 treats of the spectroscope and accessories.

Chapter 4 takes up microchemical examinations and is an extremely interesting and instructive essay on this subject containing as it does much of the original work of the author.

Chapters 5, 6, and 7 comprise the wet methods of qualitative chemical analysis, the characteristic reactions of the bases and acids of the various elements, and the methods for making and purifying the reagents employed in chemical analysis.

It is difficult to say too much in praise of this part of the work. The scheme for the systematic qualitative examination of an unknown substance is admirably described. The language is clear and intelligible and the explanations lucid without diffuseness. What are usually considered the rare elements are treated as fully as those of more common occurrence, constituting a marked difference between this work and nearly all others on qualitative analysis, and giving it a value decidedly exceptional.

With chapter 8 begins the operations employed in quantitative analysis and includes sampling, pulverizing, drying, and weighing.

Chapter 9 gives operations in the dry way; descriptions of furnaces, crucibles, etc.; fusion and fluxes. Fletcher's gas furnaces and burners are not mentioned, although in my opinion they are superior to any of those described.

Chapter 10 describes methods in the wet way. General operations including solution, evaporation, distillation and the precipitation, filtration, washing, drying, burning, and weighing of precipitates. In the description of filtering apparatus no reference is made to the Gooch crucible which to analysts in America must appear a serious omission.



Chapter 11 treats of the apparatus and general principles involved in the determination of metals by electrolysis. From the historical résumé it appears that Davy in 1808 was the first to deposit a metal by the aid of the current, he having obtained potassium in an amalgam, from potassium hydrate, and Luckow in 1869 was the first to employ electrolysis as a method for the determination and separation of metals.

Chapter 12 treats of volumetric analysis. The apparatus and solutions employed in volumetric work including a very useful section on indicators.

Chapter 13 gives color methods including an excellent description of the Dubosq colorimeter.

Chapter 14 describes gas analysis. This chapter which is very thorough includes a section on the qualitative determinations of gases, dividing them into groups of combustible and non-combustible, and under each head those that are absorbed and those not absorbed by potassium hydroxide, with tables of the reactions of the different gases under each group. The section on incompatible gases, or those that cannot exist together in a mixture, is very much to the point and is indicative of the thorough way in which M. Carnot treats every portion of his subject.

The publisher's part has been admirably done, the type is large and the pages look beautifully clear, while the cuts which are nearly all line drawings are easily understood.

It is quite impossible to mention all the admirable features of this volume, but what strikes me most forcibly is the clearness and thoroughness which characterize the descriptions of methods and the absolute mastery of detail shown throughout.

ANDREW A. BLAIR.

A TEXT-BOOK OF ELEMENTARY ANALYTICAL CHEMISTRY, QUALITATIVE AND VOLUMETRIC. BY J. H. LONG, M.S., Sc.D., Chicago: E. H. Colegrove. 1898. 278 pp. Price \$1.50.

The proper presentation of the subject of this book is always difficult, and must vary with the needs of each particular class or instructor. In general, the brief courses of qualitative analysis—the short cuts to a knowledge of the system—are dangerous and tend to loose work on the part of students in that they are led to mechanical performance of the so-called practical methods, rather than to the thoughtful, and thorough

study of the properties and reactions of the elements and compounds, which the methods themselves should serve to illustrate, and upon which they must be based. But the book before us is the sequel to a careful study of the properties of bodies and of the fundamental laws as set forth in the author's excellent work, "Elements of General Chemistry," and therefore in a larger measure free from this objection.

It is divided into two parts, Qualitative Analysis and Volumetric Analysis. In the first part the discussion of the group separations and reactions is preceded by an introduction in which the *raison d'être* for the grouping is briefly but completely and logically set forth, and the illustrative table, presented on page 5, must prove invaluable to the student by offering most comprehensively an exposition of this most important principle of analytical work.

In the discussion of each group we find first the most important and characteristic reactions of the elements constituting it, all well chosen and clearly described; and second the methods for separation of the individual elements of the group. In this latter connection most faithful attention is given to the details to be followed, and precautions to be observed at each step.

The acids are treated in the same manner as the bases and their treatment is followed by two chapters on the systematic analysis of unknown complex substances, brief, but sufficient, constant reference being made to preceding chapters.

The chapter on reactions of a few organic substances, most of the latter having pharmaceutical importance, and that on examination for poisons will find useful application.

In the second part of the work, volumetric analysis is treated in the same logical, thoughtful, painstaking way. The general theory of volumetric methods is clearly set forth and it is fully illustrated in the applications of the principles to the determination of well-known elements. These illustrative methods are followed by special methods which find extensive use, for instance for determination of sugars, starch, glycerol, and for the sanitary analysis of waters.

An appendix giving tabular schemes for the group separations and tests, tables of weights and measures, and tables of solubilities, will be found useful for reference.

The book will be particularly useful in the hands of many instructors who, like Dr. Long, have to do with students who can give but limited time to the study of chemistry and use it merely as auxiliary to the study of other subjects, as medicine, pharmacy, engineering. It is so concise, so complete, so logical in its arrangement, and so clear in the description of the reactions and methods, that our prejudice against the smaller works on these subjects is largely removed, and we are glad to commend it to the careful consideration of those instructors for whom the larger works are too bulky, and who cannot devote to the subject the time these larger works necessarily require.

W. McMURTRIE.

**LIGHTING BY ACETYLENE.** BY WM. E. GIBBS, M. E. New York: D. Van Nostrand Co. 1898. 141 pp. Price \$1.50.

This is a popular rather than a scientific exposition of the work which has been done in the effort to make artificial lighting by means of acetylene a practical success. The author in his preface claims that "the safe, efficient, and cheap lighting of houses by acetylene is an accomplished fact," a claim which many doubtless would be ready to dispute.

Short chapters are devoted to the history, dangers, and purification of acetylene; but the bulk of the volume is devoted to descriptions of electric furnaces for the production of the carbide, and generators for effecting its decomposition and the storing of the resulting acetylene gas.

Acetylene lamps and burners claim some twenty pages, and the volume closes with the requirements of the New York fire underwriters, and a list of the U. S. patents relating to this subject. Unfortunately the book has no index.

It is rather surprising to note the amount of brain power which has been devoted to the devising of acetylene generators, and yet the author assures us that "the ideal machine has certainly not yet been invented."

Most gas companies in this country would resent the author's rating of their gas at sixteen candles.

The volume will be found useful by those wishing to try acetylene lighting on a small scale, but we think its value would have been increased if the author had omitted some of the impossible generators and had said something on the details of

installing an acetylene plant, its cost, cost of the light as compared with other artificial illuminants, etc.

The volume is well printed and abundantly illustrated.

E. G. LOVE.

**A SHORT COURSE IN INORGANIC QUALITATIVE ANALYSIS FOR ENGINEERING STUDENTS.** By J. S. C. WELLS, Instructor in Analytical Chemistry, Columbia University. New York: John Wiley & Sons. 1898. vi + 294 pp.

The author of this book aims, according to the preface, to give a short but thorough course in qualitative analysis for the use of students who have only a limited time to devote to the subject.

This statement, which is frequently repeated in substance in the prefaces to laboratory manuals, and which often denotes a want of completeness in the treatment of the subject, cannot be so understood in the case of the present work.

Beginning with an excellent chapter upon reactions and the use of formulas in general, the author discusses the properties and behavior of bases towards reagents in a thoroughly satisfactory manner. Many chemical facts of general interest are interspersed throughout the book, serving to illustrate the importance of a knowledge of the reactions taught by qualitative analysis.

Equations are used more freely than in some of the larger works and will supply in advance answers to many of a student's questions. The methods directed for use in the separation of the bases of a group are, in the main, those of Fresenius, although modifications are here and there suggested which are undoubtedly to be looked upon as an advance. In his treatment of the separations of acids the author has given some good methods.

In all cases the schemes for separations are presented in the form of tables supplemented by full and detailed explanatory notes. In the part devoted to the analysis of complex mixtures the student receives many useful suggestions. A short chapter upon reagents closes the book.

Altogether, it is quite evident that, in spite of the author's modest limitation of the use of the book to engineering students, it will find a much wider use. The accuracy of treatment and completeness of detail will commend its use both to teacher and student.

F. C. PHILLIPS.

## BOOKS RECEIVED.

Crop Circular for September, 1898. United States Department of Agriculture, Washington, D. C. 4 pp.

Bulletin No. 51.—Variations in Milk and Milk Production. 28 pp. Bulletin No. 52.—Orchard Cultivation. 23 pp. Bulletin No. 53.—Abstract—the Chemistry of the Corn Kernel. 4 pp. University of Illinois, Agricultural Experiment Station, Urbana, Ill.

Bulletin No. 76.—Commercial Fertilizers. 9 pp. Bulletin No. 77.—Wheat. 14 pp. Kentucky Agricultural Experiment Station of the State College of Kentucky, Lexington, Ky.

The Fertilizing Value of Street Sweepings. An investigation made under the direction of H. W. Wiley, by Ervin E. Ewell. Bulletin No. 55. U. S. Department of Agriculture, Washington, D. C. 19 pp.

The Apple in North Carolina. A bulletin of practical information for the apple-growers of the state. Bulletin No. 149. The North Carolina Experiment Station, Raleigh, N. C.

Medicinal Plants, which have been collected and used in North Carolina. Bulletin No. 150. 89 pp. The North Carolina Agricultural Experiment Station, Raleigh, N. C.

Zur Erinnerung an R. Fresenius. Seinem verstorbenen Vater in der Zeitschrift für analytische Chemie gewidmeter nachruf von Heinrich Fresenius. Wiesbaden: C. W. Kreidel's Verlag. 1897. 18 pp., with portrait.

Geschichte des chemischen Laboratoriums zu Wiesbaden während der Zweiten 25 Jahre Seine bestehens von Professor Dr. H. Fresenius. Wiesbaden: C. W. Kreidel's Verlag. 1898. 128 pp.

Commercial Organic Analysis. A treatise on the properties, proximate analytical examination, and modes of assaying the various organic chemicals and products employed in the arts, manufactures, medicine, with concise methods for the detection and determination of their impurities, adulterations, and products of decomposition. By Alfred H. Allen, F.I.C., F.C.S. Second Edition. Revised and Enlarged. Volume IV.—Proteids and Albuminous Principles, Proteoids or Albuminoids. Philadelphia: P. Blakiston's Son & Co. 1898. 584 pp. Price \$4.50.

Essentials of Materia Medica, Therapeutics, and Prescription Writing, arranged in the form of Questions and Answers prepared especially for Students of Medicine. By Henry Morris, M.D. Fifth Edition. Philadelphia: W. B. Saunders. 1898. 288 pp. Price \$1.00.

A Text-book of Volumetric Analysis, with Special Reference to the Volumetric Processes of the Pharmacopoeia of the United States, designed for the use of Pharmacists and Pharmaceutical Students. By Henry W. Schimpf, Ph.G., M.D. Third Edition, Revised and Enlarged. New

York: John Wiley & Sons. 1898. xxviii + 522 pp., with fifty-nine illustrations. Price \$2.50.

Introduction to Chemical-Technical Analysis. By Prof. F. Ulzer and Dr. A. Fraenkel. Authorized Translation with Appendix by the Translator, Hermann Fleck, Nat. Sc. D. Philadelphia: P. Blakiston's Son & Co. 1898. vii + 188 pp. Illustrated. Price \$1.25.

Manual of Determinative Mineralogy, with an Introduction on Blow-pipe Analysis. By George J. Brush. Revised and Enlarged, with Entirely New Tables for the Determination of Minerals. By Samuel L. Penfield. Fifteenth Edition. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1898. x + 312 pp. Price \$4.00.

A Manual of Chemical Analysis, Qualitative and Quantitative. By G. S. Newth. New York: Longmans, Green & Co. 1898. xii + 462 pp. Price \$1.75.

Soaps. A practical manual of the manufacture of domestic, toilet, and other soaps. By George H. Hunt, F.C.S. Illustrated with 66 engravings. London: Scott, Greenwood & Co.; New York: D. Van Nostrand Co. 1898. xii + 385 pp. Price \$5.00.

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AMERICAN CHEMICAL SOCIETY.

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## A NEW GAS.

BY CHARLES F. BRUSH.<sup>1</sup>

Received October 25, 1898.

THE purpose of this purely preliminary paper, is to announce the discovery of a new gas; presumably elementary, and possessed of some extraordinary properties. It is a constituent of the atmosphere, and is occluded by many substances. Its chief characteristic thus far ascertained, is enormous heat conductivity at low pressures. In order to appreciate this phenomenon, it is necessary to consider the heat conductivity of some of the well-known gases.

A year ago, I had the honor to read before this section a paper on the transmission of heat by gases, illustrated by numerous curve sheets showing the heat conductivity of several gases at all pressures, from atmospheric down to the best vacuum obtainable; also an allied paper on the measurement of small gaseous pressures. Abstracts of these papers appear in the current volume of *Transactions*, and their full text may be found in the *Philosophical Magazine*, for January, 1898, and November, 1897, respectively.

The apparatus used for the described experiments in heat transmission, consisted in part, of a long-stemmed thermometer hanging in a long-necked glass bulb, the bulb of the thermometer being in the center of the glass bulb. Two bulbs were used for different experiments; the larger one 112 mm. in diameter,

<sup>1</sup> Read before the American Association for the Advancement of Science, August 23, 1898.

the smaller one only 20 mm. A tank of water and crushed ice under the bulb was adapted to be raised when desired, so as to immerse the bulb in the cold mixture. The neck of the bulb was connected with an air-pump capable of reducing the internal pressure to a very small fraction of a millionth of atmospheric pressure; also with an elaborate pressure-gauge adapted to measure small pressures with very great precision, and a barometric gauge for measuring larger pressures.

In using this apparatus, the gas to be tested was introduced at atmospheric pressure; the ice-tank was raised and the falling temperature of the thermometer, which could lose heat only by radiation, conduction, and convection through the surrounding gas, was observed through a telescope. The time required for the temperature to fall through a given range, usually from  $15^{\circ}$  to  $10^{\circ}$  C., was carefully noted. Then the ice-tank was lowered, permitting the thermometer to regain the temperature of the laboratory; some of the gas was pumped out, and the cooling of the thermometer again observed at this reduced pressure. This process was repeated many times, until the pressure was reduced to the lowest point attainable.

The results obtained with each gas were plotted in a curve showing its heat conductivity at all pressures from atmospheric down, the ordinates representing the reciprocals of the time of cooling in seconds, while the abscissas represented the pressure.

The present chart shows curves representing the heat conductivity of several gases, from fifty millionths of atmospheric pressure downward. The data for all of these except the helium curve, are taken from last year's paper; but the scale is different.

I am indebted to Prof. Ramsay for the helium used in obtaining the curve here shown.

The ordinates of each curve measured from A B as a base line, represent the total rate of heat transmission by the ether and the gas at the pressures indicated by the abscissas, while ordinates measured from the line C D, represent the heat transmitted by the gas alone.

It will be observed that the curves of all the gases named, vanish together at the point of zero pressure D. Repeated experiments have shown this condition to be always strictly true within



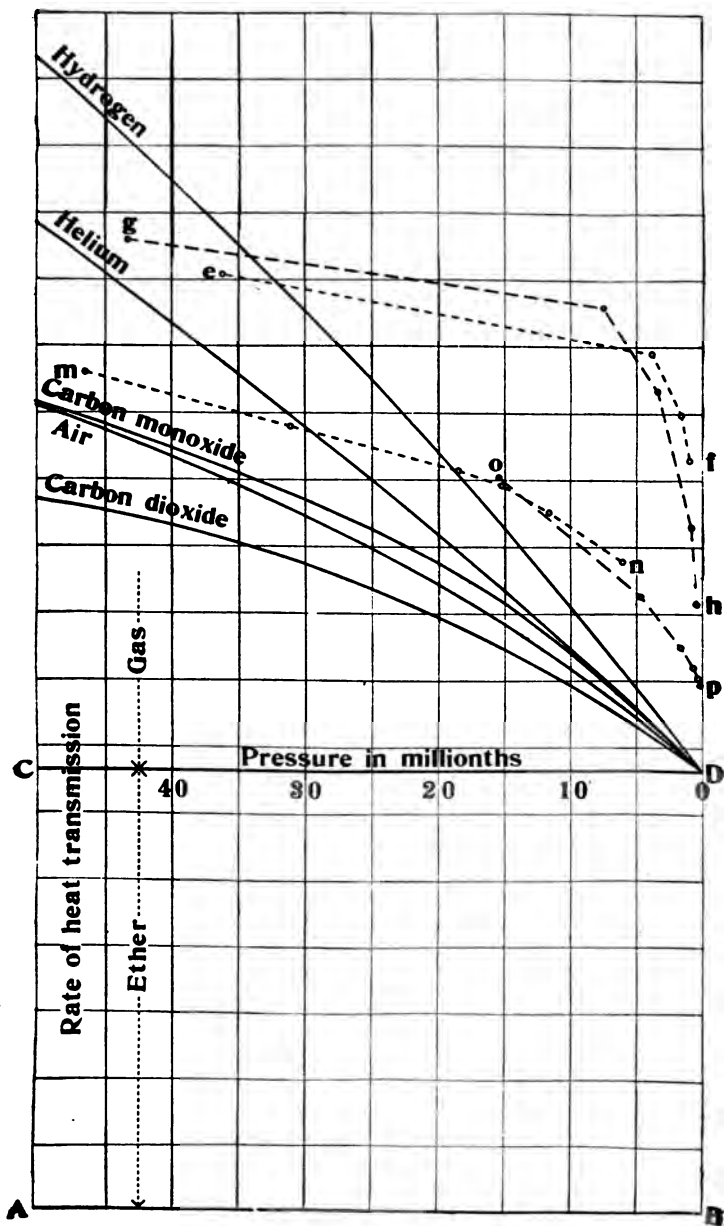


CHART SHOWING THE RELATIVE HEAT CONDUCTIVITY OF GASES.

the narrow limits of errors of observation, *provided* that before the introduction of the gas to be tested, the whole apparatus has been kept highly exhausted for several days ; or better still, has been heated several hours by means of air- and water-baths, while kept exhausted. Without one of these precautions, I was never able to get any gas curve quite down to the point D, for reasons which will appear. The point D represents a period of 300 seconds required for the temperature of the thermometer to fall from  $15^{\circ}$  to  $10^{\circ}$ , with the pressure of the surrounding gas reduced to one twenty-millionth or less.

A very brief account of the circumstances which led to the discovery of the new gas may not be out of place. I had long been engaged in high vacua experiments, and had observed that glass apparatus when highly exhausted and heated, evolved gas for an indefinite length of time—rapidly at first, then slower, but never stopped until the temperature was reduced. On cooling, rapid reabsorption always took place, but was never complete, indicating that two or more gases had been evolved by heating, one of which was not absorbed on cooling. In other words, the absorption was selective. The truth of this conclusion was abundantly demonstrated subsequently. However, the percentage of reabsorbed gas was so large, that I used a small quantity of pulverized glass in several experiments, to absorb a part of the residual gas after the highest attainable exhaustion was reached. The pulverized glass was always lead glass like that of the apparatus, and was heated nearly red hot for several hours before and during the final exhaustion.

During these experiments a curious phenomenon was noted ; the pulverized glass lost its snowy whiteness. This, I thought, must be due to reduction of some of its lead ; probably by hydrogen evolved on heating. If so, I argued that the hydrogen must have been absorbed from the atmosphere since the manufacture of the glass ; and its presence in the glass, if proven, would be a long step toward proving the normal presence of hydrogen in the atmosphere.

Following the line of experiment thus suggested, I prepared a quantity of pulverized soda glass free from lead, and placed about 120 grams of it in a large combustion tube connected with the apparatus already described. The glass was made from an

old stock of tubing, and was of such a degree of fineness that it all passed through a sieve of 90 meshes to the linear inch, but would not pass through a 140-mesh sieve. The combustion tube was adapted to be heated by a gas furnace with automatically regulated gas supply, so as to be maintained at any desired temperature.

While prepared to make analysis, in the usual way, of the gas evolved by the pulverized glass in case it appeared in sufficient quantity, I relied chiefly on its heat conductivity for the detection of any large proportion of hydrogen in the last few millionths, not being prepared at that time for spectroscopic examination; and thinking that perhaps some hydrogen might be evolved in the last stages of exhaustion before heating, I tested the conductivity of the residual air from time to time as the preliminary exhaustion progressed.

When the exhaustion approached a good vacuum, an astounding phenomenon developed. At 36 millionths pressure the residual gas conducted heat twice as well as air, and nearly as well as hydrogen; at 3.8 millionths it conducted seven times as rapidly as hydrogen; at 1.6 millionths, fourteen times, and at 0.96 of one millionth, twenty times as rapidly. These results are plotted in the curve *ef*. I did not carry the exhaustion lower than 0.96 M. At this pressure the time of cooling of the thermometer from 15° to 10° was only 177 seconds; while pure hydrogen would have required 288 seconds.

Evidently a new gas of enormous heat-conducting capacity was present, mixed with the last small portion of air. It must have come from the pulverized glass, and probably formed only a small fraction of the mixture. The last cubic centimeter of gas pumped out was collected, and upon subsequent analysis of it, nothing but air was found.

The discovery of the new gas as above outlined, was made nearly a year and a half ago, on March 10th, 1897. On the following day, the pressure had increased to nearly 5 millionths, while the time of cooling of the thermometer, instead of diminishing as usual with increase of pressure, had raised from 177 seconds to 245 seconds, showing that the new gas had largely disappeared. This was subsequently found to be due to absorption by the phosphorus pentoxide used in desiccation.

Long continued moderate heating of the pulverized glass caused the evolution of some air, much carbon dioxide and hydrogen, some carbon monoxide, and more of the new gas. The selective absorption which occurred on cooling, was confined almost wholly to the hydrogen and new gas. After further moderate heating and thorough exhaustion, I raised the temperature, continued the exhaustion, and got the results embodied in the curve *g h*, showing that much of the new gas was present; the conductivity at 0.38 millionth, the last station in the curve, being *twenty-seven times* that of hydrogen. Several days of high heating, with frequent exhaustion, failed to wholly deprive the pulverized glass of its new gas, though the output was greatly diminished. For this and other reasons, I believe that the new gas resides *in* and not simply on the surface of glass.

To make sure that the apparatus was not deceiving me, I sealed off the combustion tube, heated the vacuous parts several hours by means of air- and water-baths as before indicated, admitted air dried over phosphorus pentoxide, exhausted step by step, and got the data for the "small bulb" air curve shown here and in last year's paper. Evidently I had not been deceived about the presence of a new gas in the pulverized glass. I subsequently exposed this lot of glass several days to the atmosphere, spread out in a thin layer. When tested again after this exposure, it yielded the new gas both before and after heating, as freely as at first. This rejuvenation of pulverized glass by exposure to the air, was fully confirmed with another lot made from common window glass; and in connection with the results obtained by the diffusion of air, hereafter described, leaves no room for doubt that the new gas is a constituent of the atmosphere.

Pulverized glass appears to begin evolution of the new gas as soon as the atmospheric pressure is reduced. In one case while making a slow preliminary exhaustion, I tested the air which remained when the pressure was still 132 mm.; and to my great surprise, found it contained not only a trace, but a considerable quantity of new gas. The amount increased rapidly as the pressure was further reduced. This leads to the belief that finely pulverized glass gives up the greater part of its new gas on simple reduction of pressure to a low point, and without

heating ; somewhat as palladium gives up occluded hydrogen.

Several other substances than glass were examined, and nearly all found to contain the new gas. A specimen of old charcoal made from pine-wood sawdust by long exposure to a bright red heat, yielded, as was expected, comparatively large quantities of several gases when heated in vacuum. At some stages of the evolution these were rich in the new gas.

It would seem easy in such cases to remove the diluent gases by oxidation and absorption ; but it is not. After making the necessary additions to my apparatus, I made many attempts of this kind. The reagents used were in large excess on account of the very small quantities of gas treated ; so that some of the observed results may have been due to impurities. Cupric oxide and lead chromate evolved gases of their own almost indefinitely on high heating in vacuum, and then freely absorbed carbon dioxide and moisture at a lower temperature. Soda-lime, dried in vacuum in presence of phosphorus pentoxide, was almost indifferent to carbon dioxide. All the reagents named, especially phosphorus pentoxide, absorbed the new gas ; and all but the latter gave it up on heating.

A specimen of very fine white siliceous sand, when heated in a vacuum, gave a large quantity of gas consisting principally of hydrogen and hydrocarbons, with a considerable amount of the new gas. Some of this mixture was exposed successively to the action of red hot cupric oxide, soda-lime, and phosphorus pentoxide. By this treatment the gases were reduced to less than three per cent. of their former volume. The residue was not very rich in the new gas, because of the absorption of the latter by the soda-lime and phosphorus pentoxide, as I afterwards learned ; but I have shown the curve *op* of its heat conductivity, because the pressure was carried to a lower point than in any other case. At the last station in the curve, representing a pressure of 0.12 of a millionth, the conductivity was equal to that of 5.1 millionths, or forty-two times as much hydrogen. From this it seems reasonably certain that the curve *ef*, if carried to as low a pressure, would have shown a conductivity at least a hundred times greater than hydrogen. And yet the new gas in that experiment must have been very far from pure on account of the continuous evolution of ordinary gases, as shown by the rise of

pressure and loss of conductivity during the next few hours.

It will be observed that when the new gas was present, the form of the conductivity curves was very different from those of the known gases, the effect of the new gas becoming more prominent as the pressure was reduced. I do not doubt that this was due to the interference of the heavier and slower moving molecules of the ordinary gases always mixed with the new gas. In last year's paper I described the same effect found in a mixture of carbon dioxide and hydrogen. When the new gas is obtained in a state of purity, I expect to find its curve of heat conductivity similar to those of hydrogen and helium, but with immensely increased ordinates.

Believing that the new gas is very much lighter than air or hydrogen, and may therefore be separated from the atmosphere by successive diffusions, I have spent several months in experiments with this end in view. Quite recently my efforts have been crowned with most promising success. The difficulty has been to find a suitable porous septum; one free from holes, and sufficiently fine grained to prevent more than a very slow passage of air, while a considerable surface is exposed to the atmosphere on one side, and to a fairly good vacuum on the other. Many substances were tried. India-rubber gave encouraging results, but was capricious, and very slow. The best results have been obtained with porous porcelain having its superficial pores nearly closed by suitable treatment. A tube of this kind, closed at one end, and exposing rather more than five square inches of surface to the air, was connected with the apparatus, and the whole kept exhausted to a pressure of one and three-tenths mm. About nineteen cc. of gas were diffused per hour. After thirty-six hours the diffusion tube was shut off, the exhaustion continued, and data for the curve *mn* obtained. It was found impracticable to carry the exhaustion below six millionths, because of the presence of moisture, which interfered with the action of the pump,—no desiccating agent being used. As both phosphorus pentoxide and soda-lime absorb the new gas, they cannot be used for desiccation. If the exhaustion had been carried as far as in the curve *op*, it is probable that a higher conductivity than in that curve would have been shown; *i. e.* a conductivity more than forty-two times that of hydrogen, or some-

thing like a hundred times that of air. Here we have the heat conductivity of air at very low pressure, increased something like a hundredfold by one diffusion. I have not yet tried a secondary diffusion, but feel confident that successive diffusions of air will afford a practicable means of obtaining the new gas in a state of approximate purity.

Now let us discover, if possible, the meaning of the extraordinary heat conductivity of the new gas. I have tabulated the molecular weight, density, specific heat, mean molecular velocity, and heat conductivity of hydrogen, helium, carbon monoxide, air, and carbon dioxide, which are the known gases represented in the curve chart. For easy comparison, I have taken not only the density, but the specific heat, mean molecular velocity, and heat conductivity of hydrogen as unity. The similarity of values in the fifth and sixth columns, for molecular velocity and heat conductivity, is striking. On the chart, the curves for carbon monoxide, air, and carbon dioxide, are evidently too high to correspond well with the relative values of molecular velocity in the fifth column; but these curves represent only the last 50 millionths of the complete curves. By following these back to 500 millionths, which is still a rather small pressure, and taking their values at intervals of 10 millionths from no pressure upward, we obtain as a mean of all these values for each gas, the quantities shown in the sixth column. These agree fairly well with the molecular velocities.

COMPARISON OF GASEOUS PROPERTIES.

1	2	3	4	5	6
Gas	Molecular weight	Density D	Relative specific heat	Relative molecular velocity $\frac{1}{\sqrt{D}}$	Relative heat conductivity
Etherion	? 0.0002	? 0.0001	6000.?	100.?	100. .
Hydrogen	2.	1.	1.	1.	1.
Helium	4.	2.	? .300	0.71	0.73
Carbon monoxide	27.8	13.9	0.072	0.27	0.33
Air	28.8	14.4	0.069	0.26	0.32
Carbon dioxide	44.8	21.9	0.064	0.21	0.21

I offer the suggestion that the relatively high conductivity of the last three gases at the low pressure shown in the chart, is due to the dissociation of some of their molecules by unobstructed impact on the walls of the containing vessel, recombination being more and more retarded as the pressure is lessened, because the greater separation of the molecules reduces the frequency of collisions. Helium, perhaps because it is monatomic and therefore incapable of dissociation, has a nearly straight curve like hydrogen; and its ratio, given in the sixth column, varies but little throughout the whole range observed, which was more than 1000 millionths. I have taken the density of helium as 2; but Prof. Ramsay finds it a little less than this when purified as far as possible by repeated diffusions. This makes its relative molecular velocity a little more than 0.71, and brings it still closer to the observed value of its heat conductivity.

From the foregoing, we may reasonably conclude that the heat conductivity of gases at low pressures, and their mean molecular velocities, are closely related. Hence, if we can learn the heat conductivity of an otherwise unknown gas, we can form some idea of its mean molecular velocity; and from this, of its specific heat, density, and molecular weight.

As before indicated, the heat conductivity of the new gas at very low pressure, even when mixed with a large proportion of other gases, is something like 100 times that of hydrogen. I shall not be surprised to find the conductivity of the pure gas 1000 or more times greater than that of hydrogen; but let us be conservative, and for the present purpose call it 100 times, and see what follows. I have given it this value at the head of the sixth column.

If my inference that the heat conductivity and molecular velocity of gases are directly related is correct, then the molecular velocity of the new gas will be 100 times that of hydrogen, as shown at the head of the fifth column. As is well known, the mean molecular velocity of a gas varies directly with the square root of its absolute temperature, and is independent of pressure. The mean molecular velocity of hydrogen at the temperature of melting ice, has been found by calculation to be 5.571 feet per second. Hence the mean molecular velocity of the new gas at the same temperature will be 557.100 feet, or more than 105



miles per second. At anything like this molecular velocity, it would be quite impossible for a gas to remain in the atmosphere, *unless the space above also contained it*. A velocity of only about seven miles per second, if unchecked except by gravitation, would be sufficient to project a body from the earth permanently into space. Even at a temperature very close to absolute zero, the new gas would have sufficient molecular velocity to escape from the atmosphere.

Again, inasmuch as the molecular velocities of gases vary inversely as the square roots of their densities, it follows from our assumption of its molecular velocity, that the density of the new gas is only the 10-thousandth part that of hydrogen, as shown at the head of column 3. This is the 144-thousandth part the density of air. It is generally believed that the gases of the atmosphere distribute themselves in the long run, each as though the others were absent. Hence the new gas must extend 144-thousandth times as high as the heavy constituents of the air, to bring about the same proportionate reduction of pressure, even if gravitation remained constant at all distances from the earth; but the restraining influence of gravitation on the expansion of the atmosphere diminishes as the square of the distance from the earth's center increases. It is evident therefore, without a mathematical demonstration, that the new gas being present in the atmosphere, must extend indefinitely into space without great loss of pressure. This is only another way of stating the result of its assumed molecular velocity. Now there is no doubt that the new gas exists in the atmosphere, though probably in very small proportion; perhaps much less than a millionth. Hence it seems really probable that it not only extends far beyond the atmosphere, but fills all celestial space at a very small pressure. In recognition of this probability, I have provisionally named it aetherion or etherion, meaning "high in the heavens." Its symbol will naturally be Et.

I am aware that strong objections may well be raised to the hypothesis of an interplanetary and interstellar atmosphere; but I can see no escape from the conclusion I have drawn, if I am not mistaken in my premises.

The estimated relative specific heat of etherion appears at the head of the fourth column, based again on the assumed relative

molecular velocity. In estimating the specific heat, I have not made it inversely proportional to the density, as would be required by Dulong and Petit's law, giving a value 10,000 times that of hydrogen ; but have used the formula suggested by Prof. Risteen in his work on "Molecules and the Molecular Theory," which requires that the product of the specific heat and molecular weight of gases shall vary with the number of degrees of freedom of their molecules. I have assumed as probably true, that etherion is monatomic, with atoms possessing only three degrees of freedom.

Of course the values I have estimated for the molecular weight, density, specific heat, and molecular velocity of etherion, are intended only to indicate the *order* of magnitudes we may expect to find on further investigation ; and it must not be forgotten that they are based on two assumptions : first, that the heat conductivity of etherion is 100 times that of hydrogen ; and second, that the ratio of heat conductivity and mean molecular velocity is the same for all gases. As before indicated, I expect to find the heat conductivity of etherion much higher than the value here assigned to it. If so, the real values of its other attributes will be still more startling than those here given. The second assumption, while by no means proven, seems at least a good "first approximation" to the relation between heat conductivity and molecular velocity in gases.

There is some evidence that etherion is a mixture of at least two different gases. In the course of my experiments I have met with a great many specimens, obtained in various ways from various sources ; but always mixed with a very large excess of other gases. Some specimens were almost wholly absorbed by the phosphorus pentoxide at first used for desiccation. Others were but partially absorbed, the absorption being very rapid at first, but in an hour or two dwindling to nothing, and leaving a residue of gases permanently showing, by their heat conductivity, the presence of a very considerable amount of etherion. Soda-lime absorbed etherion, but much less freely than phosphorus pentoxide, and gave it up again on heating. The gas thus recovered was but little, if at all affected by phosphorus pentoxide.

In one experiment, the gases evolved from ten ounces of

pulverized window glass, both before and after heating, were passed through coarsely pulverized soda-lime and then over fresh phosphorus pentoxide. Not a trace of etherion remained. The same result was obtained when another lot of the siliceous sand already referred to was used as the source of etherion.

I will venture the conjecture that etherion will be found to consist of a mixture of three or more gases, forming one or more periodic groups of new elements, all very much lighter than hydrogen. If this proves true, I propose to retain the present name for the lightest one.

The transmission of radiant energy through space, has always been to me a fascinating phenomenon, and I have indulged in much speculation concerning the ether—that mysterious something, by means of which it is effected. The remarkable properties assigned to the ether from time to time in order to account for observed phenomena, have excited my keen interest; but I have long entertained the hope that some simpler explanation of the mechanism involved will be found. To me, a less strain of the imagination is required in the assumption that instead of a continuous medium, gaseous molecules of some kind, endowed perhaps with a mode or modes of motion at present unknown to us, are the agent of transmission; a gas so subtle, and existing everywhere in such small quantity, that it has escaped detection.

Perhaps the molecular hypothesis of the ether has proven so attractive to me, because it supports the hope that we may sometime compass the perfect vacuum,—a portion of space devoid of *everything*. Such a vacuum would be opaque to light, and gravitative attraction could not, I believe, act through it. It might afford a new point of view from which to study the profound mystery of gravitation; an *outside* point.

The late De Volson Wood<sup>1</sup> considered the question of a gaseous ether mathematically, and deduced certain necessary properties of the hypothetical gas, chief among which were exceedingly small density, and exceedingly high specific heat. Possibly we are about to find a gas which will fulfil the required conditions. It may be etherion, or its lightest constituent if it turns out to be a mixture. I venture to express the hope that etherion will at least account for some phenomena at present attributed to the ether.

<sup>1</sup> *Phil. Mag.*, Nov., 1895.

On account of the presumably extreme smallness of its molecules as compared with those of glass, etherion probably passes through the latter when any considerable difference of pressure exists on opposite sides; though the passage may be very slow. It seems to be condensed or compressed in glass as before indicated, and may evaporate on the side of lower pressure, and be absorbed on the side of higher pressure, after the manner of hydrogen in passing through palladium. In my own experiments, the heat transmission ascribed to the ether may be due to the presence of the new gas inside the bulb. A small fraction of a millionth would be sufficient, and this might escape detection by the pressure-gauge, on account of the necessary compression in the gauge head causing absorption by the glass. Again, etherion must always be present to some extent in all "vacuum tubes" (as well as in my own conduction bulb) on account of its long-continued evolution from glass; and may be the medium of propagation of the Roentgen rays in the vacuum glass and air.

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**ON THE FACILITIES FOR STANDARDIZING CHEMICAL  
APPARATUS AFFORDED BY FOREIGN GOVERN-  
MENTS AND OUR OWN.<sup>1</sup>**

BY LOUIS A. FISCHER.

Received October 17, 1898.

**I**T is at the invitation of your esteemed president, Dr. C. E. Munroe, that the Office of Standard Weights and Measures submits for your consideration and information this paper, stating what facilities are afforded by foreign governments and our own for the standardization of chemical apparatus. It is but proper that such information should be furnished by this Office; for it, more than any other bureau of the government, is called upon to make the determinations referred to. But before going further, a brief history of the Office will be given, in order that its position and condition may be understood.

The origin of the Office may be said to date from May 29th, 1830, when the Senate passed a resolution calling upon the Secretary of the Treasury to cause to have made a comparison of the weights and measures in use at the principal custom-houses.

<sup>1</sup> Prepared and read before the American Chemical Society, Boston, August, 1898, by direction of Dr. Henry S. Pritchett, Superintendent U. S. Coast and Geodetic Survey, and Standard Weights and Measures.

This task was entrusted to Ferdinand R. Hassler, the then superintendent of the Coast Survey, who discovered large discrepancies among the standards in use. His report led to the establishment of a shop and laboratory, in which copies of those standards adopted by the Department were made and compared. The task was entered upon by Mr. Hassler with his usual foresight and energy; and early in 1836 we find the statement in one of his reports that "forty weights, two pint measures, and four sets of yard standards are ready for final adjustment."

When we consider that the zinc used in the construction of these standards was mined and purified by Mr. Hassler; that machinery and apparatus had to be designed and built; and that the proper working force had to be organized, we cannot help admiring the tremendous energy of the man. So satisfactory were the operations that in June, 1836, Congress passed the following resolution:

*"Resolved,* That the Secretary of the Treasury be, and he hereby is, directed to cause a complete set of all the weights and measures adopted as standards, and now either made or in the progress of manufacture for the use of the several custom-houses, and for other purposes, to be delivered to the Governor of each state in the Union, or such person as he may appoint, for the use of the States, respectively, to the end that a uniform standard of weights and measures may be established throughout the Union."

For the first ten years the entire efforts of the office were devoted to the construction and verification of standards of length, weight, and capacity. These operations required the construction and investigation of comparators, balances, thermometers and barometers; and the determination of the expansion of water and metals, and the solution of other physical problems.

About 1842 the questions of hydrometers and sugars were referred to the Office, then under the direction of Prof. A. D. Bache. The exhaustive report,<sup>1</sup> made in 1848 by Prof. R. S. McCulloh, who had charge of the investigation, has become standard; and the alcoholometric tables now used by the Treas-

<sup>1</sup> Reports from the Secretary of the Treasury of Scientific Investigations in relation to Sugar and Hydrometers, by Professors Bache and McCulloh, 1846; Executive Document No. 50; 30th Congress, 1st session.

ury Department in the collection of duty on spirits differ but slightly from those submitted in the report.

The passage of the law of 1866, legalizing the Metric System, and directing that each state in the Union be supplied with copies of the metric standards, again imposed duties upon the Office which occupied its attention for many years.

In 1891, and again in 1897, the Office was represented on scientific commissions appointed for the purpose of discovering and reporting upon the cause of discrepancies in sugar determinations, by means of the polariscope, at the various ports of entry. As was suspected at the time, much of the trouble was traced to the use of erroneous standards, especially of capacity. Errors were also caused by the use of erroneous values assigned to the quartz control plates by their manufacturers; and, also, by ignoring the effect of temperature on the rotation of the sugar solutions and plates.

As a result of the report of the first commission, the Office was called upon to standardize control plates, and to devise means for rapidly verifying the large number of tubes, weights, and flasks used in sugar laboratories. No apparatus is now used by the Customs Service unless it has first been examined by the Office of Weights and Measures. Nothing illustrates the necessity of having verified apparatus more than the case just cited. In many instances flasks supposed to contain 100 Mohr cc. were found in error as much as one-half cc., and it soon became manifest that if the flasks were to be used without appreciable error they would have to be graduated by the Office. Accordingly, the arrangement here shown<sup>1</sup> was devised for graduating the flasks; and between 2,000 and 3,000 have been graduated during the past six years.

The flasks, samples of which are afterwards tested, must not show a greater error than 0.05 cc.; and no difficulty has been encountered in keeping within this limit. The Office is, therefore, prepared not only to standardize flasks, but also to mark them, provided the interior diameters of the necks do not exceed fifteen mm. or fall below ten mm. There is no reason, however, why this kind of work should be done for the general public, for the same accuracy may also be attained by

<sup>1</sup> For description of device see pages 924 et seq.

manufacturers. No special skill is required to manipulate the device used by us, and a speed of twenty flasks per hour may be maintained without extraordinary effort.

The Office of Standard Weights and Measures is not required by law to make comparisons for other than official purposes; but inasmuch as we have in our care the national standards, it has been the policy of the Office for years past to endeavor to meet all demands. Our means, however, are very limited, compared with those provided by other governments for bureaus doing similar work. Germany has its 'Physikalisch-Technische Reichsanstalt', where both scientific and technical research are carried on. This institution has two sections, the duties of which are as follows:

#### SECTION I.

1. The performance of physical investigations and measurements which tend, preeminently, to the solution of physical problems of great scope and importance in a theoretical or practical direction, and which demand a greater outlay of instrumental equipment, consumption of material, or time of observers and computers, than can, as a rule, be offered by private individuals or educational institutions.

2. The solution of matters referred to it by Section II, in so far as the equipment of the latter is insufficient for their accomplishment.

#### SECTION II.

1. The execution of such physical or physico-technical investigations as are directed by *official authorities* or designed to promote precise machine construction, or other branches of German industry.

2. Verification of measuring apparatus and instruments of control, so far as they do *not* lie in the domain of weights and measures; the determination of the errors of graduation of such instruments, and the issuance of certificates of results.

3. Construction of instruments and parts of instruments, as well as the execution of other mechanical work for German state institutions and authorities, in so far as their construction by private workshops gives rise to difficulties.

4. In special cases the construction of parts of instruments for

Germans in business, in so far as their construction in private shops necessitates extraordinary means.

In all cases where work is done for individuals or for foreign governments charges are made, designed to cover the cost to the Reichsanstalt. In order to meet the demands there were regularly employed in 1897 seventy-eight persons, many of the scientific attachés being men of international reputation.

The purely weights and measures matters of the Empire are under the control of the Kaiserliche Normal-Aichungs Kommission, with a central office in Berlin, and three branches at Köln, Ilmenau, and Gehlberg, respectively. The commission prescribes rigorous rules and regulations concerning the construction and verification of all forms of measuring apparatus, chemical included, and also defines the tolerance or allowable errors. If the tolerance be not exceeded, and the apparatus otherwise conforms with requirements, it receives the stamp of the commission, and may then be used anywhere in Germany.

Austria, likewise, has its Normal-Aichungs Kommission, with duties and authorities similar to those of its German prototype.

In England the supervision of weights and measures is the work of the Standards Department of the Board of Trade. The verification of every weight and measure is provided for by law, and penalties are prescribed for using apparatus not in conformity with the regulations of the Standards Department.

The inspectors, who in 1897 numbered 1099, are appointed by local authorities, but are required to work under regulations provided by the central office.

In addition to having under its control the standards, which include those of electricity, the office collects information in regard to weights and measures in foreign countries, which is published in its regular reports. Authority is also given to the Board of Trade by law "to conduct all such comparisons, verifications, and other operations with reference to weights and measures, in aid of scientific researches or otherwise, as it may deem expedient."

The Kew Observatory, also, has a standardizing department, and in 1897 about 300 hydrometers, and over 20,000 thermometers, were examined there. Provision is also made for experi-



ments and researches in connection with the work of the various departments of the observatory, and considerable experimental work has been done with platinum thermometers at high temperatures with gratifying results.

Recently a committee was appointed by the British Government "to consider and report upon the desirability of establishing a National Physical Laboratory for the testing and verification of instruments for physical investigation, for the construction and preservation of standards of measurement, and for the systematic determination of physical constants and numerical data useful for scientific and industrial purposes; and to report whether the work of such an institution, if established, could be associated with any testing or standardizing work already performed wholly or in part at public cost." The consideration of this question by the government is due, no doubt, to the demands of scientific investigators, who are at present much inconvenienced by being compelled to resort to Berlin or Paris when the more refined comparisons are required. It is also largely due to the fact that the Reichsanstalt has, by reason of its high standing, done much to assist the German manufacturer in disposing of scientific apparatus.

In France the national standards are in the care of the Conservatoire des Arts et Métiers in Paris, where splendid facilities are provided for the comparison of other standards with them. All trade weights and measures are verified at suboffices, of which there is a large number. While the suboffices are under the control of the Verification Department of the Conservatoire, and while that department is required to verify their standards at regular intervals, it is not required to do their work, but is left free to undertake the more refined comparisons demanded by those engaged in technical and scientific investigations.

Splendidly equipped laboratories for various branches of technology are under the control of the Conservatoire, and these laboratories are at the service of engineers, constructors, and others who desire to use them. The reports of the Conservatoire do not indicate that *special* provisions or regulations are provided for the standardization of chemical apparatus, and the same statement applies to the British institutions. This is no doubt due to the fact that the demand for this character of work is not sufficient to make special facilities necessary.

This brief résumé of the means provided for the standardization of measuring apparatus by the principal governments makes manifest our own deficiencies. It was plainly the intention of Congress, when in 1836, and again in 1866, it directed the distribution of standards to the states, that each state should establish an office where at least the commercial weights and measures could be verified. This is actually the case in but few states, and the Office of Standard Weights and Measures, with an appropriation of less than \$8,000,<sup>1</sup> is called upon to standardize county and city weights and measures, and also do other work plainly not that of a national office. The result of this condition of affairs is that the more important investigations and verifications demanded by chemists, physicists, and engineers, are made to suffer. But even if our whole efforts could be devoted to the character of work referred to, our means would be entirely incommensurate with the requirements of a country whose industrial and scientific progress during the last two decades has been, to say the least, extraordinary.

However, this is a matter for Congress to decide; and until that body deems it proper to provide better means, the Office will continue to make the best use of those at hand.

For the benefit of those who desire more detailed information, the following description of our methods and apparatus is given:

#### WEIGHTS.

Two copies of the "International Kilogramme," both of which are identical in form and material with that prototype, are in the custody of the Office. We have, also, a kilogram balance, constructed by Rueprecht of Vienna, by means of which the relation of two kilograms may be determined within their one hundred millionth part.

For smaller weights we have a set of the best chemical balances on the market; and by making and computing the weighings in the manner indicated in Appendix No. 10, U. S. Coast and Geodetic Survey report for 1892, we are able to secure more than necessary accuracy, say 0.001 of a milligram for a milligram weight. The appendix referred to gives the least square adjustment of the weighings, which are so arranged as to bring

<sup>1</sup> About one-third of this amount is for the electrical department.

a precise result.<sup>1</sup> With the aid of this publication, and with the largest weight of such sets as are commonly used properly determined, any chemist may determine his smaller weights.

While all of those present are aware that weights and other bodies are buoyed up by the air, all do not perhaps, realize, the magnitude of the effect produced. We are led to make this statement by the complaints frequently made by chemists and assayers that the values given by this Office are incorrect. The International Kilogramme is a standard of *mass*, and hence, to express the values of other masses in terms of it, the weighings are referred to *vacuo*. If, therefore, some of the weights of a set are made of brass and some of platinum, the values given are not those that would be found by unreduced weighings made in the air. The difficulty would not be overcome by referring the weighings to air under standard conditions, for if the weights were compared at, say Leadville, at an elevation of 10,000 feet, they would not agree with results obtained at lower altitudes. The difference for 10,000 feet would be, if the weights were platinum and brass, about  $\frac{3}{100}$  of a milligram per gram, a quantity which a good chemical balance would readily show. Agreement of the *weights* under all conditions would be secured if they were all made of one metal, and, for many reasons, platinum is to be preferred, at least for weights of one gram and less, where the cost of the metal would not be a matter of much consequence.

Some years ago the Office adopted an official stamp, which is placed upon weights meeting the following requirements:

- (a) Each weight must be made of one piece of metal.
- (b) The weights, if brass, must not be lacquered, but should be gold-plated or platinized.
- (c) The finish must be such as to readily show any abrasion, either accidental or otherwise.

#### VOLUMETRIC DETERMINATION.

No special facilities are required for this kind of work. Furnished with a set of weights, a balance, a thermometer, distilled water, and a table of densities of water, any one may determine his

<sup>1</sup> By this statement is meant that the most reliable results, obtainable from the particular set of observations, are deduced. If the observations are poor the results are correspondingly so.

own apparatus. The reduction to *vacuo* of weighings may be made with sufficient accuracy by assuming that a liter of air weighs one and two-tenths grams at sea-level, and diminishes 0.04 gram for each 1,000 feet of elevation. The density of the weights, if of brass, may be taken as 8.3; if of platinum, as 21.5. This data will certainly satisfy all requirements when dealing with apparatus, the capacity of which is determined by filling or emptying to a mark.

The reduction to *vacuo*, under normal conditions, affects the result by about 0.10 of a per cent., if brass weights be used to weigh the water; and by about 0.11 of a per cent. if platinum weights be used. It is evident that if the result is affected by only 0.01 of a per cent. in changing from one metal to another whose density is two and a half times greater, no appreciable error can possibly be introduced by assuming the densities given above.

Likewise, the assumed weight of air is not subject to variations of more than five per cent., and hence the reduction to *vacuo* (which, as before stated, affects the final result by about one-tenth of a per cent.), is not affected by more than 0.005 of a per cent. by probable variation in the weight of air adopted. In calibrating specific gravity bottles, and capacity measures provided with ground-glass covers, greater accuracy is, and may be, attained; and an accuracy of one part in 100,000 is not too much to expect, if verified weights and thermometers are used, and if the proper precautions be taken.

In all the work of the Office the capacities are, for convenience, originally found in milliliters, and if the measures are graduated according to some other system the proper factor is used to convert into that system. The liter referred to was defined by The International Committee of Weights and Measures in 1880, in the following language:

"The International Committee of Weights and Measures adopts for its publications and official use the word 'litre' to express the volume of a kilogramme of pure water at its maximum density."

A recently completed determination of the mass of a cubic decimeter of water, made at the International Bureau, confirms what was suspected by the committee when the above definition

was adopted; namely, that the original determination, made a century ago, was in error. The recent results indicate that the liter is larger than the cubic decimeter by one-tenth of a milliliter, or 0.01 of a per cent. This difference may be ignored for most purposes, and the cubic centimeter and milliliter still be considered synonymous terms; but when we adopt a unit of volume we should be careful to distinguish between the two.

#### THERMOMETRY.

All temperatures are referred to the standard hydrogen thermometer of the International Bureau of Weights and Measures by means of mercurial thermometers made by Tonnelot, of Paris, and compared directly with the hydrogen thermometer. These thermometers give us a continuous range of  $80^{\circ}\text{C}.$ ; from  $-28^{\circ}$  to  $+52^{\circ}$ , with a sufficient degree of accuracy to more than satisfy our ordinary needs.

Thermometers submitted for verification are placed between two standards in a trough filled with water, which is thoroughly mixed by propellers operated by the observer, just before the readings are made. Means are provided for rapidly raising and lowering the temperature of the water in the trough, by letting in either cold or hot water, as the case requires. The indications of the thermometers are read by means of a low power microscope, which may readily be moved into position over each instrument. Some idea of the accuracy with which the readings are made, and also of the uniformity in temperature of the water in the trough, may be formed from the statement that after the readings of the two standards have been corrected<sup>1</sup> they do not differ on the average by more than  $0.005^{\circ}$ , a quantity which cannot be read on any but the most perfect instrument.

Considerable experimental work has been done at the International Bureau with thermometers at temperatures as low as  $-70^{\circ}\text{C}.$ , and also between  $+100^{\circ}$  and  $+200^{\circ}$ ; but, as yet, the work is not complete. As soon as it has been finished the United States will acquire, like other contributing governments, copies

<sup>1</sup> The corrections consist of the calibration corrections for inequality of bore; the correction for errors in graduation of the stem; the zero correction, which depends upon the temperature to which the thermometer has been exposed; the correction for exterior pressure on the bulb, which depends upon the height of the barometer; the correction for internal pressure (if the thermometer be in a vertical position), which depends upon the height of the column of mercury in the stem; and finally, the reduction to the standard hydrogen scale.

of the new thermometers, and our range will then be correspondingly extended. Recent results obtained with the so-called platinum thermometers in England and on the Continent, lead us to hope that this range will soon be much extended. At present, however, the Office is compelled to limit the comparison of thermometers to temperatures between  $0^{\circ}$  and  $+50^{\circ}$  C., and the following rules will govern the acceptance of thermometers for verification :

- (a) The stem and bulb must be made of one piece of glass.
- (b) The graduation must be ruled directly upon the stem.
- (c) The graduation lines must not exceed in width one-tenth of the space between them.
- (d) The graduations must not be more than  $1^{\circ}$  apart.
- (e) The upper part of the capillary tube must be enlarged ; that is, there should be a small chamber in it.

These requirements are essential, even in thermometers of ordinary precision ; and until they are fulfilled by our manufacturers, those requiring instruments of superior construction will continue to seek them abroad.

#### POLARISCOPIC APPARATUS.

Quartz control plates, polariscope tubes, and polariscopes are also examined for sugar chemists, by the Office. Control plates, to be accepted, must be free from imperfections, and must be properly mounted. The values will then be determined by comparison with the standard plate of the Treasury Department. This plate has the value,  $99.06^{\circ}$  on a scale, the  $100^{\circ}$  point of which is determined by a solution of pure sugar and water at a temperature of  $17.5^{\circ}$  C., that contains a mass of 26.048 grams of sugar per 100 milliliters of solution. This solution differs slightly from that used in Germany to determine the  $100^{\circ}$  point of the Ventzke Scale ; but if the samples of sugar be polarized as prescribed by the Treasury Department regulations, and with apparatus tested by the Office of Weights and Measures, the results will agree with those obtained by the German method with German apparatus. If the solutions are made up and polarized at any other temperature than  $17.5^{\circ}$  C., the effect of temperature must, of course, be considered. The report of the commission of 1897 has not yet been made public, but I under-

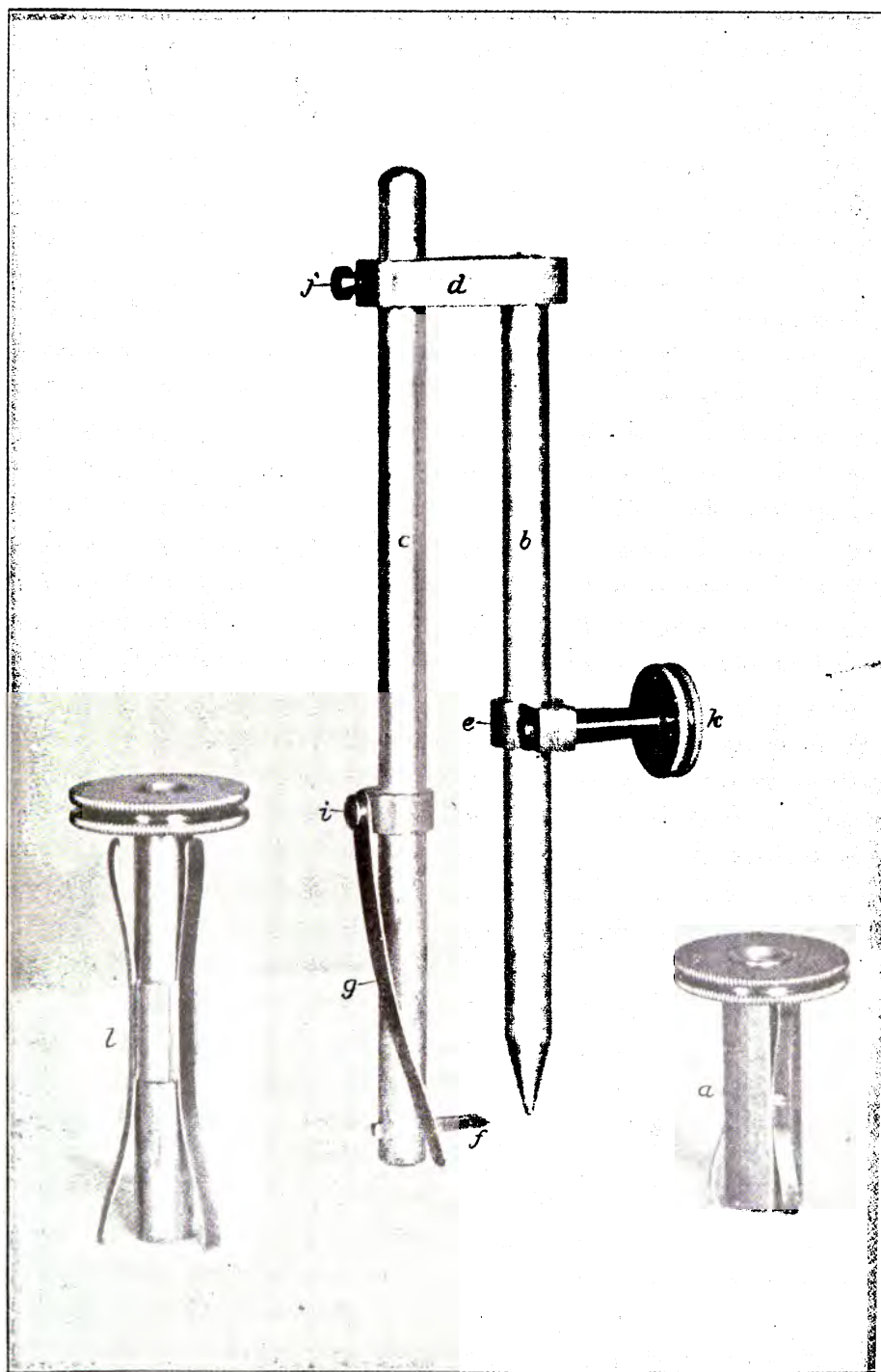
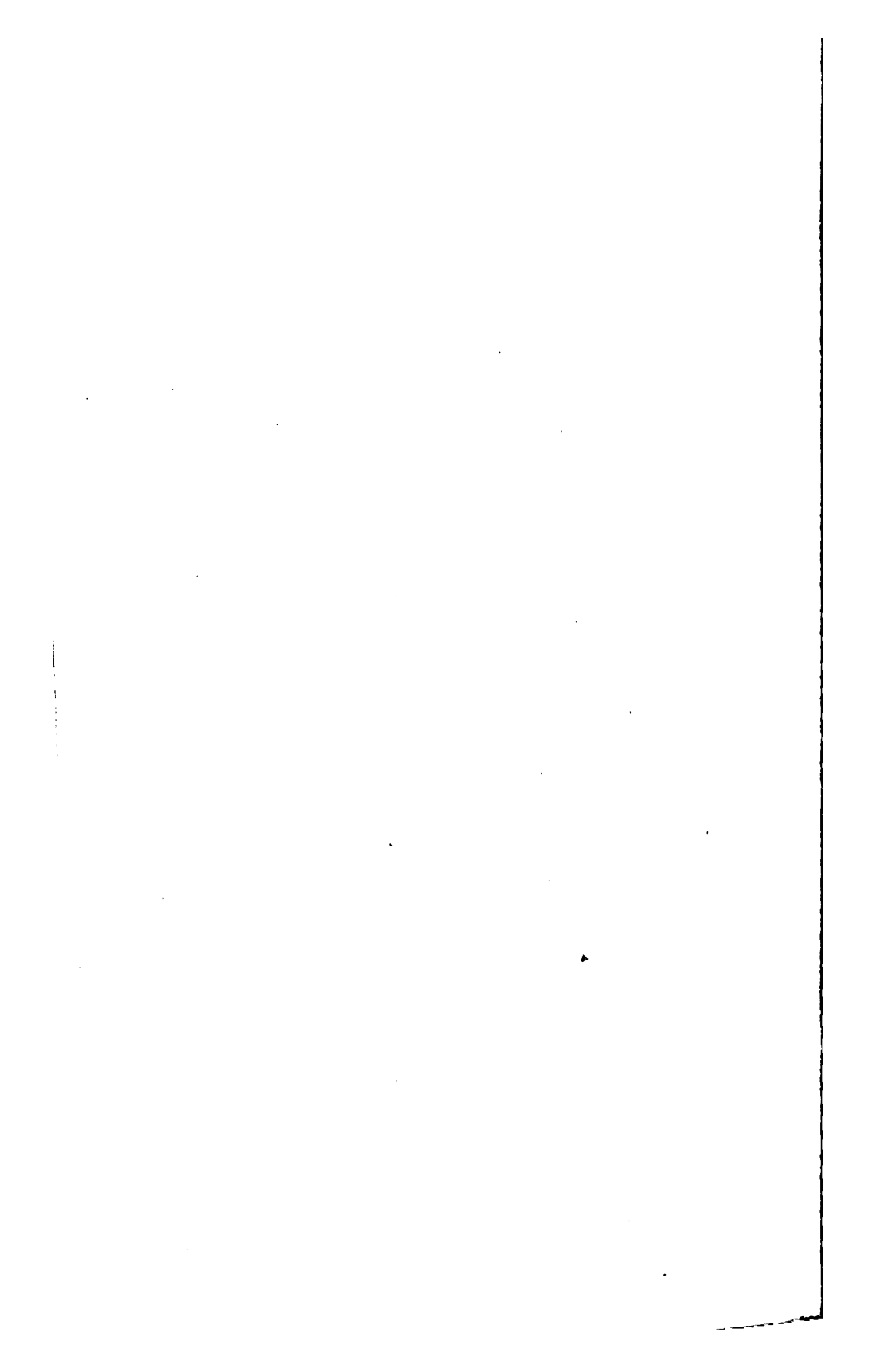


Fig. 1.





stand that the question of bringing our methods, as well as results, into accord with the Germans, was considered.

#### HYDROMETERS.

Hydrometers, graduated according to various authorities, are used in this country, but no tables of densities corresponding to the graduations have been adopted, except in certain cases by the Treasury Department for its own use. For this reason the table to be used must be designated by those submitting their instruments. The Baumé hydrometers are used, perhaps, more than any others in this country, and the statement made in 1831 by Prof. C. F. Chandler in a report to the National Academy of Sciences is as true now as it was then. His statement was as follows: "Although Baumé described, with great accuracy, the method which he employed to secure the scale for his hydrometers, and it would seem, therefore, as though no difficulty existed to prevent the reproduction of his instruments, nevertheless, it is a fact that among instrument makers the scale has been so modified from time to time that we have the greatest variety of instruments purporting to be Baumé, each one of which has a set of degrees of an entirely different value from that exhibited by any other. I have found twenty-three different scales published by as many different writers for liquids heavier than water, the highest of which gives as the value of 66 Baumé, 1.8922, and the lowest 1.730, no one of which can be said to be correct, or to have been obtained by following Baumé's directions." At the conclusion of this report he offered the following resolution: "*Resolved*, That a committee be appointed to consider what action, if any, is desirable, with a view to establishing a legal value for the degrees of the Baumé and other hydrometers of arbitrary scale, the committee to report at the next meeting." A committee was appointed, but I have been unable to find any report made by it.

It has often been suggested that the only safe plan would be to abandon all arbitrary scales and to use only instruments which record the true densities. This proposition is usually opposed by the so-called practical men; but I see no reason why such instruments should not be used for scientific purposes. We already have in use by the U.S. Coast and Geodetic Survey, and

by the U. S. Fish Commission, hydrometers so graduated, and I have never heard of any complaint from those who are required to use them. What is wanted is the density of sea-water, and the instruments give it directly.

If the apparatus submitted for verification were limited to certain forms, and if the limit of error were in every case stated, the work of the Office would be simplified. We are, therefore, much interested in the movement inaugurated by this society to secure uniformity in the more important measuring apparatus used by chemists, and would be pleased to cooperate with the society in bringing about the desired result. Of course, measuring instruments of all kinds must be designed, primarily, to suit the needs of those who use them, but the uncertainties introduced by having them graduated according to various systems and standardized at various temperatures does not serve any good purpose.

In conclusion, I beg leave to recommend that the following units of measurement be adopted by the society, as they already have been by almost the entire scientific world.

(1) The liter, as defined by the International Committee of Weights and Measures; *viz.*, the volume of the *mass* of a kilogram of pure water at the temperature of maximum density, and under a pressure of 760 mm. of mercury.

(2) Density, defined as the ratio of the mass of a substance to that of an equal volume of pure water at its maximum density ( $4^{\circ}\text{C.}$ ).

(3) The centigrade degree of the hydrogen thermometer of the International Bureau of Weights and Measures.

I also recommend that some convenient temperature be adopted, at which all volumetric apparatus shall contain their stated capacities.

#### DESCRIPTION OF DEVICE FOR MARKING FLASKS.

Referring to Fig. 1, *a* is a hollow steel cylinder which fits into the neck of the flask where it is held and centered by the three springs shown in the figure. Its upper end is terminated by a milled head which must be in contact with the top of the flask whenever the device is in use. The diameter of the opening in *a* is such that the rod *b* fits in it without play. *b* and *c* are round rods

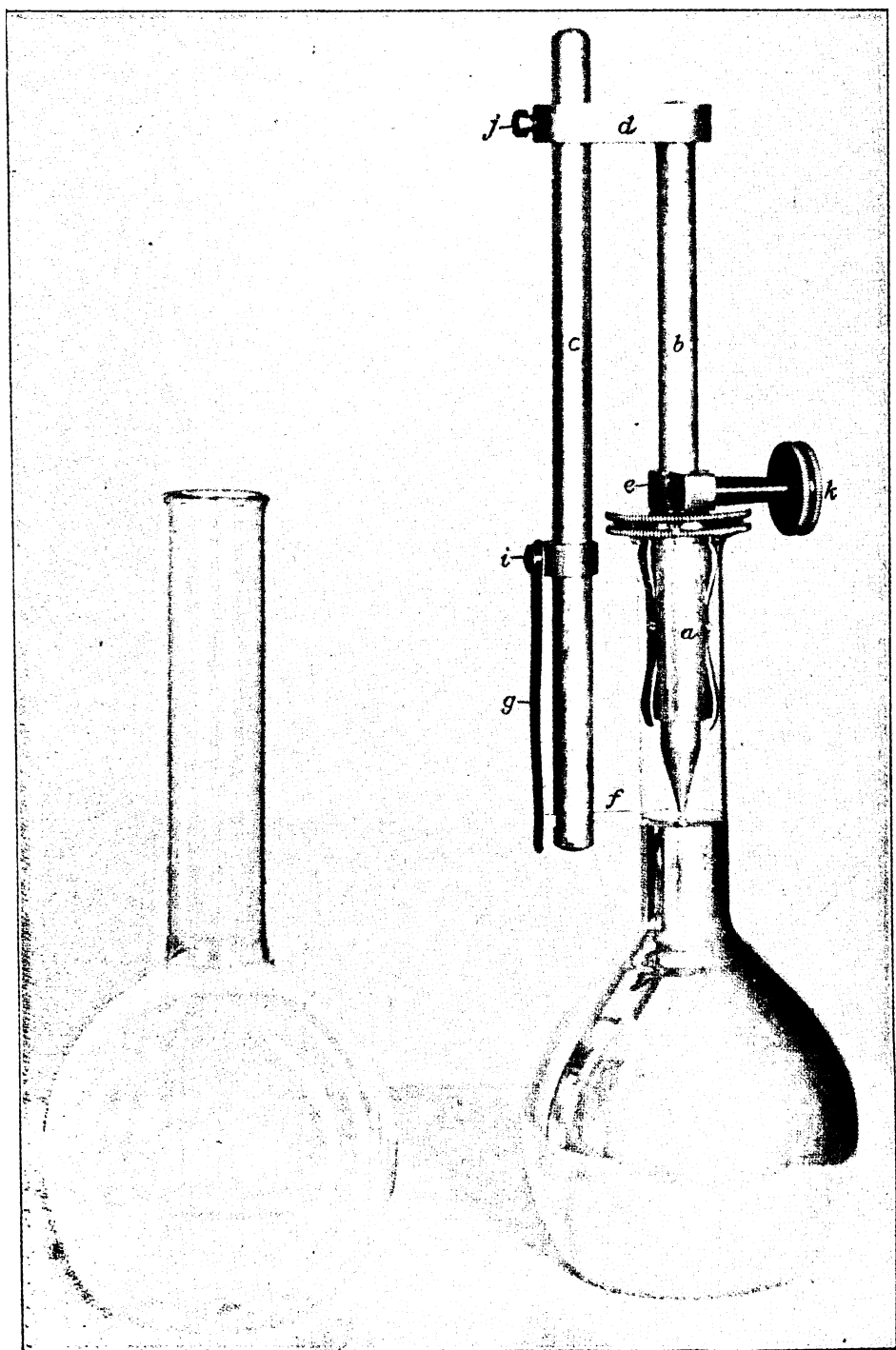
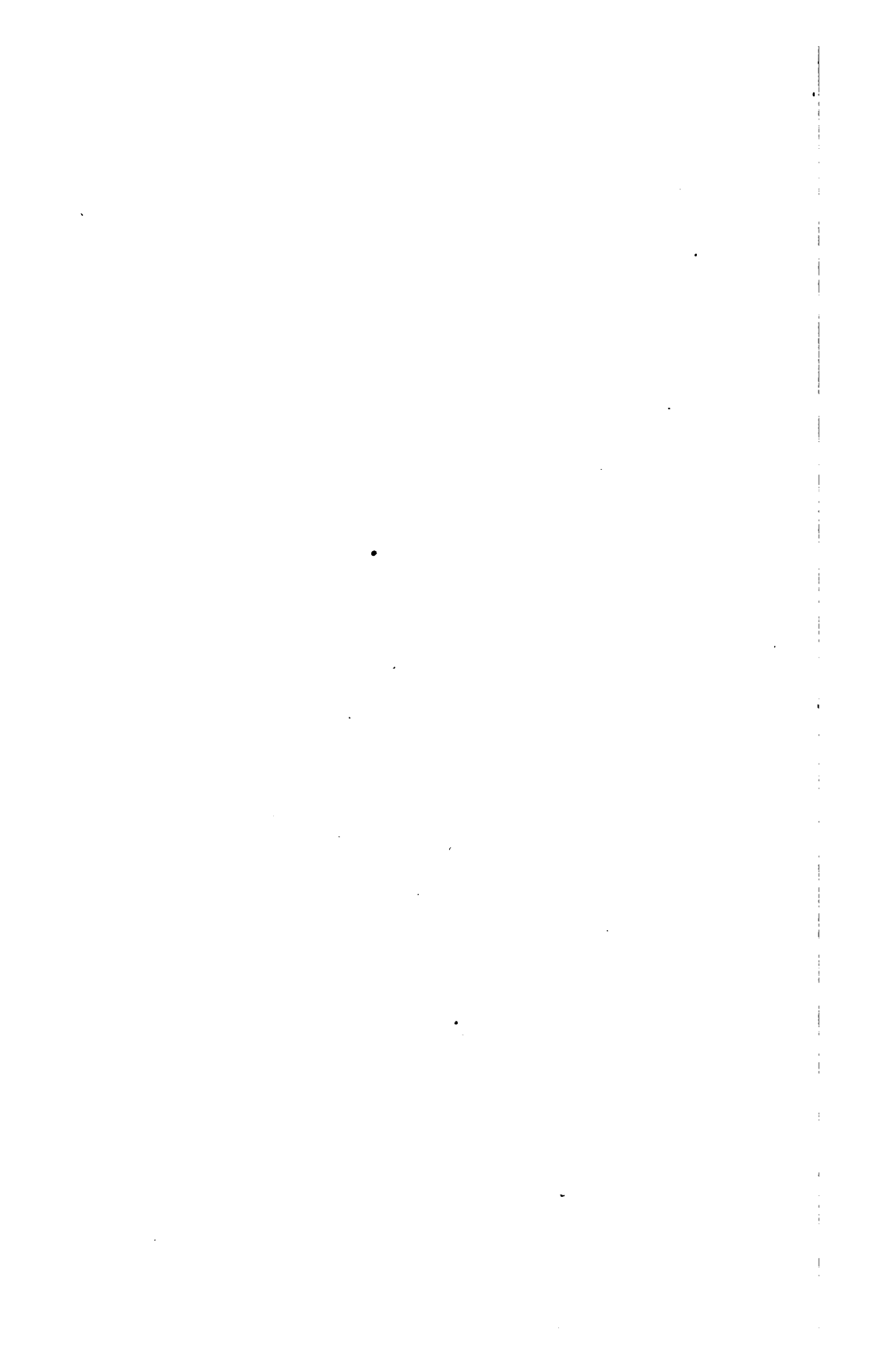


Fig. 2.



made of Stubbs' steel, parallel to one another and rigidly connected by *d*. The cutter *f* is made of square steel, and while it must slide freely back and forth in the opening provided for it in *c* it must not have appreciable side play. By means of the screw *j* which clamps *c* to *d* the height of the cutter must be adjusted so that the edge of the cutter operates in the horizontal plane tangent to the pointed end of *b*. The clamp *e* forms a stop on *b* and may be clamped at any point by the screw *k*. The spring *g* is swivelled at *i* and its function is to press the cutter towards *b*. *l* is an extra bearing for flasks having necks of smaller diameter than could accommodate *a*.

The operation of marking is illustrated in Fig. 2. The flask on the right represents a standard, which is essential as the device is only designed to reproduce the volume of some flask assumed to be correct. The standard is represented filled with mercury up to the point where it is tangent to the lower end of *b*. The order of operation is as follows: The bearing *a* or *l* as the case requires is pushed into the neck of the empty *standard* until the milled head comes in contact with the top of the flask. Then the rod *b* of the device is put in the bearing and pushed down until the cutter falls into the mark on the neck of the flask. The clamp *e*, which should always be kept in contact with the upper end of the bearing, is then clamped. The device may now be rotated in the bearing and if this be done the cutter will follow the mark on the neck. The whole arrangement is now removed from the neck of the standard and clean mercury is poured in until it fills the flask to the mark. This may be determined by putting the arrangement back in its original position in the standard and if the mercury is tangent to the lower end of *b* we have in the proper quantity. This is not, however, an easy matter to accomplish, but sometimes requires a little skill and patience. If the clamp *e* has not been disturbed the cutter will still travel in the mark when the mercury has been adjusted to tangency. Having secured the proper quantity of mercury the whole arrangement is again removed from the neck of the standard, and the mercury is poured into the flask to be graduated. Usually there will be a number of air bubbles in the second flask which must be removed before we attempt to mark it. Having removed the air bubbles, which must be done without raising



each form of flask to be marked. This may always be readily accomplished by placing a temporary mark on any flask and then determining the capacity to this mark. With this and the interior diameter of the neck of the flask known we may compute where the mark should be placed to give the correct capacity. When this point has been determined a permanent mark may be made with the device by adjusting the cutter to travel across this point.

The use of this method of marking flasks is restricted on account of the pressure exerted by the mercury on the walls of the flasks, which is sometimes sufficient to cause them to break. This does not occur often with 100 cc. flasks, but it is doubtful whether ordinary flasks of greater capacity than 500 cc. would sustain the pressure with safety.

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### THE CYCLICAL LAW OF THE ELEMENTS.<sup>1</sup>

BY THOMAS BAYLEY.

Received September 7, 1898.

WHEN the elements are arranged in a line in the order of their atomic weights, it is apparent that there is from lithium to fluorine an orderly transition from the intensely positive alkali-metal type to the intensely negative halogen type, and then a sudden reappearance of the positive type in sodium, after which there is a second orderly transition to the negative type (chlorine), and then another change to positivity (potassium). Up to this point, therefore, two complete cyclical changes have been established, the first cycle from lithium to sodium—in all its essential details—being analogous with the second from sodium to potassium. If then we proceed with the lineal arrangement, it is clear that we must first of all look for transitions and for reappearances of the alkali-metal type; in other words, for the continued development of the cyclical arrangement. And since analogous but modified transitions actually recur, and halogens followed by alkali metals reappear, it is evident that the law of progression is actually cyclical. The first and fundamental feature of atomic progression is a progression in cycles.<sup>2</sup> The lithium-sodium cycle is a cycle involving the seven elements, lithium, beryllium, boron, carbon, nitrogen, oxygen, and fluorine,

<sup>1</sup> Reprinted from *Chemical News*, April 7, 1898.

<sup>2</sup> Bayley: *Phil. Mag.*, January, 1882.

the temperature greatly, the bearing is placed in the neck of the flask and the point of *b* is adjusted to tangency by means of the stop *c*. The neck of the flask in the vicinity of the cutter is then covered with paraffin by means of a camel's hair brush which is kept for the purpose in a dish of melted paraffin. The paraffin will cool almost instantly, and as soon as it does the spring *g*, which has heretofore been to one side of the cutter, is now adjusted to press the cutter against the paraffined flask. The arrangement is then rotated in the bearing and the cutter removes the paraffin in its course and exposes the glass. After a couple of revolutions the spring is pushed to one side, the cutter pulled back, and the whole arrangement removed from the neck of the flask which is now ready for etching. The mercury may be poured back into the standard in order to test whether its volume has changed by reason of the handling it has received. Usually such tests will show an increase in the volume of mercury, which must again be adjusted before it is used to mark another flask. If, however, we have a number of flasks to graduate, the volume of the mercury will be found quite constant after the first half-dozen have been marked, due to the fact that it finally acquires a fixed temperature, which is determined by the amount of handling it receives and the temperature of the room. After this state is reached, ten or a dozen flasks may be marked without the volume of the mercury being appreciably changed. The etching is done by applying hydrofluoric acid to the cut in the paraffin by means of a small camel's hair brush. The flask is then set aside for about ten minutes, when the acid is washed off with water. Finally the neck is heated over a Bunsen burner and the paraffin is wiped off with a cloth.

The arrangement here described was devised for the special purpose of marking the 100 cc. flasks used by the United States Treasury Department. The interior diameter of the cylindrical portion of these flasks (the necks) is approximately thirteen mm. Any variation of this diameter from that of the standard flask introduces an error in the capacity of the marked flask, due to the fact that the height of the meniscus of the mercury depends, within certain limits, upon the diameter of the tube containing it. It is therefore important that a standard be provided for



each form of flask to be marked. This may always be readily accomplished by placing a temporary mark on any flask and then determining the capacity to this mark. With this and the interior diameter of the neck of the flask known we may compute where the mark should be placed to give the correct capacity. When this point has been determined a permanent mark may be made with the device by adjusting the cutter to travel across this point.

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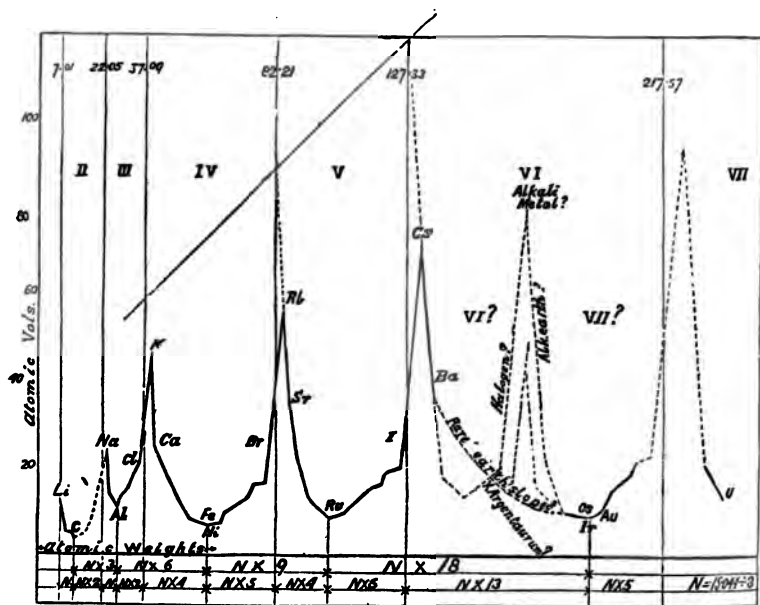
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and the sodium-potassium cycle involves also seven elements; and for this reason, and because in the succeeding cycles analogous groups of seven elements are repeated, almost all tabular expressions of the atomic progression have been set in a septenary form. But these arrangements, by unduly emphasizing the septenary character of the periodic change, have perhaps somewhat obscured the more important and fundamental cyclical features of the progression. Before attempting to substantiate this assertion, however, it is necessary to consider the nature of the higher cycles which are complex, and to show that the properties of any element are more profoundly modified by position in the cycle than by position in the septenary series.



Assuming that hydrogen is the first element of an incompletely known cycle which we may call the first, then the lithium-sodium cycle becomes the second and the sodium-potassium cycle becomes the third. Beyond this point the cycles are complex, and the fourth contains seventeen elements, of which the first, potassium, is completely analogous with sodium; the second element, calcium, with magnesium; and the third, scandium, with aluminum; for sodium and potassium both conform

to the alkali metal type, calcium and magnesium to the alkaline earth metal type, and aluminum and scandium to the type of the earth metals; but the analogies between silicon and titanium, and between phosphorus and vanadium, are less perfect, while the analogies between oxygen and chromium and between chlorine and manganese are very much less pronounced. The analogies between the latter pairs, indeed, appear to consist chiefly in structural resemblances between the compounds of the respective elements, due to the valency or atomicity impressed upon the septenary series as a primary law of its formation. The analogies between the elements of the septenary series entirely constituting the second and third simple cycles, and the elements constituting the first portion of the fourth cycle, a compound cycle, are perfect therefore only in the first, second, and third elements of each series respectively, and become fainter in the later members. Now the elements between which complete analogy exists are those which have analogous positions in the cycle, and the elements between which incomplete analogy exists are those which have not analogous cyclic position, but merely analogous serial position. The region of the third cycle—occupied by sodium, magnesium, and aluminum—corresponds to the region occupied by potassium, calcium, and scandium in the fourth cycle for each group of elements occupies the front portion of its cycle, whereas silicon, phosphorus, and sulphur in the third cycle occupy a region posterior to the point of lowest atomic volume, while titanium, vanadium, and chromium occupy a region anterior to the point of lowest atomic volume in the fourth. Neglecting for the moment the position and properties of the three intermediate elements, iron, nickel, and cobalt, and passing to the consideration of the second septenary series, which completes the fourth cycle, and to comparison of this with the third cycle, we see that analogy fails, or is chiefly structural, between copper and sodium, between zinc and magnesium, between gallium and aluminum, but becomes more pronounced between selenium and sulphur, and perfect between bromine and chlorine. The structurally analogous copper and sodium have nothing in common except serial position, and the fully analogous bromine and chlorine have similar cyclic position; chlorine fails to find a complete analogue in manganese which has not analogous

regional position, but finds it in bromine, because both occur at the end of the cycle. To make this clearer it is necessary to study more closely the architecture of the simple and complex cycles. The increment of atomic weight occupied by the series lithium-sodium is 15.98; the increment from sodium to potassium is 16.05; the increment from potassium to iron is 16.86; the increment from copper to rubidium is 22; the increment from rubidium to ruthenium is 16.2; and the increment from silver to cesium is 25.04. The increments for the series constituting the simple cycles, and for the series occurring in the first portions of the fourth and fifth cycles, is, therefore, about 16 (or 17), and the increment for the series occurring in the posterior halves of the fourth and fifth cycles is 22 and 25. If we proceed to consider the nature of the sixth cycle, we are met at the outset by a difficulty, for since no alkali metal of higher atomic weight than cesium has yet been discovered, it is not easy to fix the upper limit of the cycle.

The usual arrangement of the elements in odd and even series, such as Mendeléeff's original classification or Brauner's modification of it, show three septenary series and an intermediate group between cesium and osmium, and the increment of 57 in atomic weight corresponding to this space is just about what would be required for twenty-four elements. Commencing with potassium and writing its higher analogues in a line, we obtain the sequence potassium, copper, rubidium, silver, cesium, in which each alkali metal is followed by a subfamily analogue, and, unless other conditions intervene in the sixth cycle, the unknown element of atomic weight c. 156 should be an analogue of copper and silver, and the unknown element of atomic weight c. 170 should be an alkali metal and the first member of a seventh cycle. But as every alkali metal is preceded by a halogen (neglecting the argon family), and succeeded by an alkaline earth metal, it also follows that the element of atomic weight 170 should be similarly accompanied. Reasoning also from analogy, we must suppose that the unknown halogen is somewhat less negative than iodine, because negativity decreases with atomic weight in the halogen family, and the unknown alkali metal and the alkaline earth metal must be more positive than cesium and barium, respectively, because positivity increases with atomic

weight in the highly positive families. It also seems necessary, from analogy, to assume the existence of an intermediate group between 152 and 154, but in all other instances, both lower and higher, in the atomic progression the intermediate groups are preceded not by basic earth metals (such as samarium), but by elements such as chromium and manganese, molybdenum and (—c. 100), and tantalum and tungsten, which form oxides of a pronounced acidic character. If, therefore, there is a cycle stretching from cesium to the position of atomic weight 170, it must differ essentially from compound cycles below it and the compound cycle above it. We may now profitably turn to a consideration of the curves of atomic volume in the various cycles. It was first pointed out by L. Meyer that atomic volume has a periodic variation, and the curves given in the accompanying figure are essentially identical with those drawn in his "*Modern Theories of Chemistry*."

It is evident that atomic volume is a cyclical function. Each cycle, simple or compound, shows a loop, and all truly analogous elements occupy similar positions on the curves. The alkali metals have high atomic volumes, and occupy the top of the curves; the alkaline earth metals invariably occur on the downward flanks. The earth metals occur lower down on the same flank, and in the fourth and fifth angles they immediately precede the elements (titanium, vanadium, chromium, manganese), (zirconium, niobium, molybdenum,—), which form acidic oxides. The intermediate groups occupy the troughs of the curves, and the series copper-bromine, silver-iodine, gold-bismuth occur on the rising posterior portion of the curves. If, then, the element of atomic weight c. 170 is an alkali metal, it is reasonable to conclude that it has a high atomic volume and that curve of atomic volume indicated by the upper dotted line must exist, even if it does not follow—however probable it may appear—that this curve need necessarily be as steep as it is drawn. The curves of atomic volume present very remarkable regularities, using the word curve to mean the collection of straight lines drawn from point to point. Thus the lines drawn from chlorine to potassium, from bromine to ruthenium, and from iodine to cesium, are almost exactly parallel, as are some other lines of similar character.

In the earlier diagrams, before the atomic volume of cesium was determined, the line from iodine to cesium was assumed to occupy a position in accordance with this parallelism, and the facts when determined justified the assumption, and for these reasons it seems permissible to use this method of drawing parallel lines as a means of forecasting the atomic volumes of elements as yet undiscovered. Now, whether we draw the upper or the lower dotted curve, in which latter case the metal (atomic weight c. 170) would not be a perfect analogue of sodium and potassium, it appears necessary to believe in the existence of a halogen and an alkaline earth metal, and also of a group of intermediate elements of the iron or platinoid type, followed by a series commencing with a true analogue of copper and silver. It is a significant fact that, although a number of elements are assigned to positions between atomic weight 150 and the atomic weights of tantalum and tungsten, there has as yet been described no element corresponding to the hypothetical intermediate group, or to the supposed halogen, alkali metal, or alkaline earth metal. On the other hand, the numerous elements between atomic weight 150 and tantalum which have been described are elements of a purely earth-forming type, separable from well-located earths, such as scandium, yttrium, and lanthanum, which they closely resemble, only by repeated fractional precipitations or similar methods. So far research has not rendered it possible to assign definite atomic weights to the majority of these rare earth metals, and much of the brilliant laborious work done upon them by Crookes and others has tended rather to bewilderment, yttrium and samarium, and several other rare earth metals, having been shown to be complex bodies; but accepting the usual location of these metals provisionally, it would seem that  $Tb > Er > Tm > Yb$  fall just where the hypothetical alkali metal of atomic weight c. 170 would require to be placed, and that with these four elements there is a regular but small progression from greater to less basicity in the order given, which is what we might expect if the sixth cycle stretches from cesium to about atomic weight 233 with a long flank on the anterior (descending) portion of its curve of atomic volume occupied by a series of rare earth metals. This conception of the cyclic progression eliminates the unsym-

metrical dotted curve, and substitutes a cycle of approximately symmetrical dimensions. The cyclical increments then appear as

Cycle II.	Cycle III.	Cycle IV.	Cycle V.	Cycle VI.
c. 16	c. 16	$46(3 \times 16)$	$47(3 \times 16)$	$94(6 \times 16)$

and the position of lowest atomic volume, which in the lower cycles occurs near the middle of the curve, occupies in the sixth cycle a position nearer to the end. In these measurements of the length of the cycles, we have taken the increments of atomic weight from one alkali metal to the next higher in progression, but it does not necessarily follow that this is the proper method. For if the elements have been produced, as was suggested by Sir William Crookes, during the cooling of some primal form of matter—the protyle—we may imagine that after the genesis of each cycle had been completed, and the halogen had been formed, there came a turning-point in the evolution, probably marked by the development of an element of the argon type, after which the course of atomic genesis again set in the direction of alkali-metal formation. If so, then clearly the cycle commenced at this turning-point, but the first element of the new series may not have been formed immediately. The conditions at the commencement of the cycle may not have permitted of the coherence of the newly condensed material into the atomic form, and the first element of the new cycle may, as it were, have had to wait until the attractive force of the condensed protyle had time to gather. Some such conception might explain a lateness in the appearance of an element like argon, endowed with little or no affinity; for if the element were all the while forming in a kind of nebulous intermediate condition, and if, as it appears, atomic weight is a function chiefly or wholly of the temperature at the moment of atomic formation, such an element might not take the atomic form until after the commencement of the next cycle. This, however, assumes some sort of connection between the attraction of the primal molecules for each other and the chemical affinity of the completed atom. Before we can attempt to fix the true dimensions of the cycles in accordance with this hypothesis, we must cast about for evidences of definite arithmetical dimensions in other regions of the cycles than the beginnings. The point of lowest atomic volume seems to be another definite turning-point in the cyclic

changes; and taking carbon as representing this point in the second cycle, and iridium the similar point in the (large) sixth, we get an interval of atomic weight of 180.5. Dividing this by 12 we obtain 15.04, and adding this number to the atomic weight of carbon (11.97) the sum is 27.01, the atomic weight of aluminum (27.02), the element of lowest atomic volume in this cycle. By adding to aluminum (27.01) the expression  $15.04 \times 2$ , we obtain 57.09, which is between iron (55.9) and nickel (58.6) and the addition of  $15.04 \times 2$  again gives 102.24, which is very near the atomic weight of ruthenium (102.7); and adding  $15.04 \times 6$  to 102.24 gives 192.48, which is the atomic weight of iridium. Now assuming this dimension 15.04 to represent the true dimension of a simple cycle, and adding it to lithium, we have  $7.01 + 15.04 = 22.05$ , between fluorine and sodium, as the initial or turning-point for Cycle III. In like manner,  $22.05 + 15.04$  gives 37.09, between chlorine and potassium, as the initial-point of Cycle IV;  $37.09 + 15.04 \times 3$  gives 82.21 between bromine and rubidium, for the corresponding point of the fourth cycle, and  $82.21 + 15.04 \times 3$  gives 127.33, between iodine and cesium for the sixth cycle. If the sixth cycle is a large cycle  $127.33 + 15.04 \times 6$  indicates 217.57 as its probable terminating point. If the cyclic dimensions be fixed in this manner, the point of lowest atomic volume in the various cycles occurs in the second or third at the one-third distance, and in the fourth and fifth at the four-ninths distance from the initial point of the cycles. Thus:

$$\begin{aligned} \text{Li } 7.01 + \frac{15.04}{3} &= 12.01 \text{ (C = 11.97),} \\ 22.05 + \frac{15.04}{3} &= 27.02 \text{ (Al = 27.01),} \\ 37.09 + \frac{15.04}{3} \times 4 &= 57.13 \text{ (Fe = 55.9; Ni = 58.6),} \\ 82.21 + \frac{15.04}{3} \times 4 &= 102.25 \text{ (Ru = 102.7),} \\ 127.33 + \frac{15.04}{3} \times 13 &= 192.46 \text{ (Ir = 192.5).} \end{aligned}$$

It may be assumed that the actual turning-point of lowest atomic volume may not be occupied by an element having the atomic weight corresponding to the temperature existing when the evolutionary crisis arrived.



## ATOMIC VOLUME AS A PERIODIC FUNCTION.

By THOMAS BAYLEY.

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IN a communication to the *Chemical News* (April 7, 1898),<sup>1</sup> the author showed that between each halogen and the next succeeding alkali metal there is a point of atomic weight that may be assumed to indicate the commencement of a cycle. This point, on the hypothesis of atomic condensation from cooling protyle, marks the temperature, expressed in terms of atomic weight, at which the tide of evolution turned and the conditions began again to necessitate the appearance of the positive atoms inaugurating a new cycle. It was shown that if the size of the cycles be reckoned from the "critical" points, the measurements are regular, and that each cycle corresponds exactly to an increment of atomic weight equal to  $15.044 \times x$ ,  $x$  being one of the integers<sup>2</sup> 1, 1; 3, 3; 6, 6, taken consecutively. The apparent irregularity in the cyclic dimensions thus disappears, but the sequence of the individual elements remains unchanged and the increments of atomic weight between each atom and its next neighbor still appear to be quite irregular. But in saying that the elements occur irregularly, we merely assert that they do not appear at equal intervals, and the absence of this empirical regularity does not imply the absence of law. The study of atomic volume, on the contrary, discloses some interesting relations between the elements and suggests a definite influence ruling their occurrence. The atomic volume of an element is the result of the action of one of the fundamental forces with which the atom is endowed; this force is the attraction of cohesion between atoms of like kind. Atomic volume is thus a very important property of the elements, and if any general relations exist between atomic volumes it is desirable that they should be shown. The accompanying chart of atomic volume has been prepared and abscissae have been drawn through the "critical" points, marking the cyclic boundaries. These "critical lines" are, for the sake of easy reference, marked with letters, the lines through atomic weight 7.01 being called *A*; the line through atomic weight 22.05, *B*; through 37.09, *C*; through 82.21, *D*;

<sup>1</sup> See the preceding paper.

<sup>2</sup> The series 1, 3, 6, ..., is such that each term is made up of the sums of the natural numbers 1, 2, 3, 4, 5, 6, etc.

through 127.33, *E*; through 217.57, *F*; and the line through 307.83, *G*. Points corresponding to atomic volumes 30, 60, 90, 120, 150, etc., have been marked off on the line *A*, and lines parallel to the ordinate have been drawn through these points cutting the critical lines at right angles. The "critical intersections" of these horizontal lines with the critical lines are referred to as *A*<sub>∞</sub>, *B*<sub>∞</sub>, *C*<sub>∞</sub>, *D*<sub>∞</sub>, etc. It is possible to draw through various critical intersections a series of straight lines, each of which passes also through the points of atomic volume of two elements on the chart. The lines that can be so drawn are given below under the heading I. It will be seen that they are "analogous lines," that is, they pass through atom analogues in every instance. The coincidences of lines and points although not mathematically exact are very close approximations, even when the scale of the chart is so large as one-tenth inch per unit of atomic weight and atomic volume. This is a notable fact when one considers that the determinations of density have been made at different temperatures, and compared with water at different temperatures, and that even if the determinations had been made at a standard temperature this would still have lain at varying distances from their respective melting-points, and that a certain influence upon atomic volume must be credited to the forces of crystallization, to allotropy, etc. In addition to the lines through the "critical intersections" a large number of analogous lines can be drawn through *three* elements. These are given under the second heading (II). In a number of instances the lines cross in an element, thus locating it both as regards atomic weight and atomic volume; and by following out the system of analogous lines it is possible to tentatively assign atomic volume where this is not known, as has been done with scandium (atomic weight 44), yttrium (atomic weight 89.6), and fluorine, and furthermore to tentatively fix both the atomic weight and atomic volume of unknown elements, such as eka-tellurium (atomic weight 2212), VII<sup>1</sup>, VII<sup>11</sup>, VII<sup>111</sup>, etc. It has proved possible to construct a portion of an assumed eight cycle of dimensions  $15.044 \times 6$ , although elements of so high atomic weight have never been discovered, and to locate elements along the "rare earth slope" in cycle VI. It is not necessary, however, either to assert or deny the

actual existence of elements having the positives thus assigned, although some of them, such as eka-tellurium, VII<sup>I</sup>, VII<sup>II</sup>, VII<sup>III</sup>, all of lower atomic weight than thorium, probably occur somewhere in nature. It is enough to recognize a general relationship between the elements, as revealed in a geometrical form by the particular method herein described. Of the elements on the "rare earth slope" it may be said that if they should be found to occur as they are placed they would be in lineal analogy with the known elements, and that although it will probably ultimately be possible to classify them in the usual groups their properties will be found to be so greatly dominated by their position in the earth region of cycle VI that the structural resemblance between their compounds and the compounds of their analogues in the lower cycles will be obscure.

The atomic volumes of hydrogen, nitrogen, and oxygen have been published while this investigation was in progress, and these elements have been found to fall into the system of lines. The accompanying table shows the atomic weights and atomic volumes which have been used in setting out the chart.

The existence of a series of points positionally interrelated by lines such as those here described appears to be of mathematical interest independently of reference to any special chemical significance.

## I.

## THROUGH AN INTERSECTION AND TWO ELEMENTS.

Intersection.	Group I.	Group II.	Group III.	Group IV.
<i>B</i> <sub>30</sub>	Na	Mg		
<i>C</i> <sub>90</sub>	K	Ca		
<i>D</i> <sub>90</sub>	Rb	Sr		
<i>E</i> <sub>120</sub>	Cs	Ba	La	
<i>F</i> <sub>120</sub>	VII <sup>I</sup> (223.7)	VII <sup>II</sup> (228.2)	VII <sup>III</sup> (230.8.)	Th
<i>G</i> <sub>120</sub>	VIII <sup>I</sup> ( )	VIII <sup>II</sup> ( )	VIII <sup>III</sup> ( )	VIII <sup>IV</sup>
<i>E</i> <sub>60</sub>	Li	Ca		
<i>G</i> <sub>60</sub>	Na	Ca		
<i>F</i> <sub>30</sub>	K	Ba		
Same line {	<i>A</i> <sub>60</sub>	Rb	VII <sup>II</sup>	
	<i>A</i> <sub>60</sub>	Rb	VIII <sup>II</sup>	
	<i>F</i> <sub>120</sub>	Cu	Sr	
<i>D</i> <sub>30</sub>	VII <sup>I</sup>	Be		
<i>G</i> <sub>120</sub>	VII <sup>I</sup>	(154.5 <sup>II</sup> )		
<i>B</i> <sub>60</sub>	(151.7 <sup>I</sup> )	(154.5 <sup>II</sup> )		
Same line {	<i>C</i> <sub>210</sub>	Cs	(179.3 <sup>II</sup> )	
	<i>C</i> <sub>210</sub>	(169.4 <sup>I</sup> )	(179.3 <sup>II</sup> )	

Intersection.	Group I.	Group II.	Group III.	Group IV.
$C_{150}$	Cs	Hg		
$G_{60}$	H	VII <sup>II</sup>		
$A_{30}$	(169.4 <sup>I</sup> )	Hg		
$E_{30}$	Cr(291.1)	Sr		

In addition to those above :

	Intersection.	Group II.	Group III.	Group IV.
	$B_{60}$	Ca	Sc	
	$D_{60}$	Sr	Yt	Zr
Same line {	$E_{30}$	Mg	Sc	
	$E_{30}$	Mg	Yt	
	$D_{30}$	Be	Sc	
	$A_{30}$	Ca	In	
	$F_{90}$	Zn	Ga	
	$F_{150}$	Cd	In	
Same line {	$G_{30}$	(154.5 <sup>II</sup> )	(159.4 <sup>III</sup> )	
	$G_{30}$	(154.5 <sup>II</sup> )	Al	
	$A_{30}$	(171.3 <sup>II</sup> )	(173.7 <sup>III</sup> )	
	$D_{30}$	Hg	(159.4 <sup>III</sup> )	
	$G_{150}$	VII <sup>II</sup>	Tl	

In addition to the above :

Intersection.	Group III.	Group IV.
$A_{60}$	Sc	Ti
$C_{120}$	La	Ce
$C_{210}$	(173.7 <sup>III</sup> )	(175.6 <sup>IV</sup> )
$G_{60}$	Al	Zr
$G_{30}$	B	(161.3 <sup>IV</sup> )
$B_{90}$	(159.4 <sup>III</sup> )	(175.6 <sup>IV</sup> )
$B_{30}$	Yt	(161.3 <sup>IV</sup> )
$G_{30}$	(173.7 <sup>III</sup> )	Th
$F_{30}$	VII <sup>III</sup>	VIII <sup>IV</sup>
$B_{30}$	La	Pb
$F_{90}$	Ga	Ge
$G_{60}$	Tl	Pb

Intersection.	Group V	Group VI.
$A_{60}$	V	Cr
$C_{90}$	Nb	Mo
$B_{60}$	pr Di	W
$D_{180}$	(166 <sup>V</sup> )	(167 <sup>VI</sup> )
$C_{240}$	VII <sup>V</sup>	U
$C_{90}$	pr Di	ne Di
$B_{30}$	Sb	W
$B_{30}$	Nb	Mo
$D_{30}$	VII <sup>V</sup>	(212 <sup>VI</sup> )
$G_{30}$	(166 <sup>V</sup> )	(212 <sup>VI</sup> )

Intersection.	Group V.	Group VI.
$F_{30}$	V	pr Di
$C_{60}$	Ta	(167 <sup>VI</sup> )
$A_{120}$	Ta	W
Intersection.	Group II.	Group VI.
$E_{120}$	Ca	S
$E_{120}$	Sr	Se
$B_{60}$	Sr	Te
$B_{60}$	Ba	(212 <sup>VI</sup> )
$B_{60}$	(154.5 <sup>II</sup> )	(167 <sup>VI</sup> )
$D_{150}$	Ba	ne Di
$B_{30}$	Ca	Mo
$B_{210}$	Sr	Mo
$G_{180}$	VII <sup>II</sup>	(212 <sup>VI</sup> )
$E_{30}$	Sr	(212 <sup>VI</sup> )
$C_{60}$	(154.5) <sup>II</sup>	W
$F_{150}$	Ba	Te
$G_{90}$	VII <sup>II</sup>	(167 <sup>VI</sup> )
$G_{30}$	Mg	O
$G_{30}$	Cd	Cr
$F_{30}$	Zn	Cr
Intersection.	Group VII.	Group IV.
$A_{30}$	F?	Ti
$A_{30}$	Cl	Sn
$A_{30}$	Br	Ce
$A_{30}$	(147.5 <sup>VII</sup> )	Pb
$A_{60}$	(214.8 <sup>VII</sup> )	Th
$C_{30}$	I	Th
$G_{90}$	(214.8 <sup>VIII</sup> )	Ti
$B_{30}$	Br	(161.3 <sup>IV</sup> )
Intersection.	Group IV.	Group VII.
$G_0$	Sn	F?
$G_0$	Zr	Cl
$F_{30}$	Sn	Mn (approx.)
$G_{60}$	Sn	(99.9 <sup>VII</sup> )
$A_{30}$	Zr	(168.8 <sup>VII</sup> )
Same line {	Th	(168.8 <sup>VII</sup> )
	Pb	(168.8 <sup>VII</sup> )
	(161.3 <sup>IV</sup> )	(186.7 <sup>VII</sup> )
Intersection.	Group I.	Group I.
$F_{120}$	H	Rb
$A_{30}$	Na	Cu
$A_{60}$	Cs	VII <sup>I</sup>
$B_{90}$	Rb	(151.7 <sup>I</sup> )
$C_{210}$	Cs	(169.4 <sup>I</sup> )
$D_{90}$	K	Li
$G_{180}$	Rb	Li
$C_{30}$	VII <sup>I</sup>	VIII <sup>I</sup>

Intersection.	Intersection.	Group I.
$D_{180}$	$C_{80}$	Na
$G_{80}$	$E_{80}$	K
$A_{240}$	$B_{150}$	K
$C_{150}$	$D_{80}$	Rb
$C_{150}$	$D_{80}$	Ag
$G_{110}$	$E_{80}$	Cu
$C_{80}$	$G_{80}$	Cs
$A_{240}$	$E_{150}$	VII <sup>I</sup>
$A_{180}$	$C_{150}$	(169.4 <sup>I</sup> )
$B_{150}$	$D_{80}$	(151.7 <sup>I</sup> )
$E_{80}$	$E_{80}$	Au
$G_0 F_{80}$	$E_{120} (D_{150}) (C_{180})$	Cr
$A_{150}$	$E_{120}$	VIII <sup>I</sup>

## II.

## THROUGH THREE ELEMENTS.

Group I.	Group III.	Group I.
Li	Al	Cu
H	Ga	Ag
Cu	Tl	Ag
Ag	Al	Au
Li	Ga	Cr(291.1 <sup>I</sup> )
(151.7 <sup>I</sup> )	Tl	Cr
(151.7 <sup>I</sup> )	La	(169.4 <sup>I</sup> ) (approx.)
Li	In	(169.4 <sup>I</sup> )

NOTE.—In this group of lines Li is the only element of Group I having alkali-metal properties, the other elements of Group I being, for the most part, members of the subfamily.

	Group I.	Group II.	Group II.
	H	Mg	Cd
	Li	(171.3 <sup>II</sup> )	Hg
	Rb	Ca	Be
Same line {	Na	Ca	Ba
	approx. { Na	Ca	VII <sup>II</sup>
	K	Sr	(154.5 <sup>II</sup> )
	Rb	VII <sup>II</sup>	VIII <sup>II</sup>
	VIII <sup>I</sup>	Ba	Mg
	Cu	(154.5 <sup>II</sup> )	VIII <sup>II</sup>
	Cr	Cd	Mg
	Au	(154.5 <sup>II</sup> )	Sr
	(151.7 <sup>I</sup> )	Zn	VIII <sup>II</sup>
Same line {	(169.4 <sup>I</sup> )	Cd	Zn
	(169.4 <sup>I</sup> )	Cd	Be
	(169.4 <sup>I</sup> )	Zn	Be
	(169.4 <sup>I</sup> )	Ca	Hg (approx.)

	Group I.	Group V.	Group II.
	H	P (amorph.)	(171.3 <sup>II</sup> )
	Li	P	VIII <sup>II</sup>
	Cu	V	Mg
	Li	Nb	Hg
	Li	Sb	(154.5 <sup>II</sup> )
	Na	Sb	(171.3 <sup>II</sup> )
		(166 <sup>V</sup> )	(154.5 <sup>II</sup> )
Same line <sup>1</sup>	{ K	pr Di	Sr
	{ K	pr Di	(154.5 <sup>II</sup> )
	{ K	(166 <sup>V</sup> )	Sr
Same line <sup>1</sup>	{ Au	(166 <sup>V</sup> )	Sr
	{ Au	pr Di	Sr
	Au	Sb	Ca
	Ag	Nb	Ca
	Au	As	Mg
	Au	VII <sup>V</sup>	VIII <sup>II</sup>
	Cr	Nb	Mg
	Cr	Bi	Sr
	(151.7 <sup>I</sup> )	P	Mg
	Group II.	Group III.	Group III.
	Mg	Sc	Yt
Same line	{ Sr	Sc	Al
	{ Sr	Al	B
	{ Sr	Sc	B
	Cd	Ga	Al
	Mg	La	VII <sup>III</sup>
Nearly coincident	{ Be	(159.4 <sup>III</sup> )	VIII <sup>III</sup>
	{ (154.5 <sup>II</sup> )	(159.4 <sup>III</sup> )	VIII <sup>III</sup>
	Cd	(159.4 <sup>III</sup> )	VII <sup>III</sup>
	Be	Ga	VII <sup>III</sup>
	Sr	La	(173.7 <sup>III</sup> )
Same line	{ Hg	(173.7 <sup>III</sup> )	Al
	{ Hg	(173.7 <sup>III</sup> )	Ga
	{ Hg	Ga	Al
	{ Cd	Ga	Al
	{ Cd	Al	(173.7 <sup>III</sup> )
	(171.3 <sup>II</sup> )	(173.7 <sup>III</sup> )	Yt
	Hg	La	(159.4 <sup>III</sup> )
	Ca	Yt	La
	VII <sup>II</sup>	In	La
	Zn	In	VII <sup>III</sup>
	Be	In	VIII <sup>III</sup>

<sup>1</sup> This line passes through K, Sr, I, pr Di (154.5<sup>II</sup>), (166<sup>V</sup>), Au, and forms several combinations besides these four; *e. g.*, K, Sr, (154.5<sup>II</sup>); K, I, Au; Au 154.5, Sr; Au (166<sup>V</sup>), pr Di, etc. Several similar lines exist.

	Group II. VIII <sup>II</sup> VIII <sup>II</sup> (154.5 <sup>II</sup> ) (171.3 <sup>II</sup> )	Group III. La VII <sup>III</sup> In Ga	Group III. Al (159.4 <sup>III</sup> ) B Al
	Group IV. Ti 'Si 'Si C Ge Ce Same line { C C (161.3 <sup>IV</sup> ) Pb Pb Th Same line { Th (161.3 <sup>IV</sup> ) (161.3 <sup>IV</sup> ) Th Sn Same line { VIII <sup>IV</sup> VIII <sup>IV</sup> VIII <sup>IV</sup> VIII <sup>IV</sup>	Group V. Sb As Nb Nb Sb V V As (166 <sup>V</sup> ) Sb Nb pr Di As As Nb (166 <sup>V</sup> ) Nb VII <sup>V</sup> VII <sup>V</sup> Sb Bi	Group III. (159.4 <sup>III</sup> ) (173.7 <sup>III</sup> ) (173.7 <sup>III</sup> ) VII <sup>III</sup> VIII <sup>III</sup> B La La Tl (approx.) Sc Al Yt Al Al Ga Ga B (173.7 <sup>III</sup> ) Tl (159.4 <sup>III</sup> ) In
	Group II. Same line { Mg Mg VIII <sup>II</sup> Ca Hg Be	Group IV. Ge (175.6 <sup>IV</sup> ) Sn Zr (161.3 <sup>IV</sup> ) Zn	Group II. Cd Cd Zn (171.3 <sup>II</sup> ) Ca VIII <sup>IV</sup>
	Group II. Be Be Ca Ca Sr Cd Zn VIII <sup>II</sup>	Group IV. Ge (161.3 <sup>IV</sup> ) Zr Ce (175.6 <sup>IV</sup> ) Ti (175.6 <sup>IV</sup> ) Th	Group VI. Te (212 <sup>VI</sup> ) (167 <sup>VI</sup> ) ne Di W O U W

<sup>1</sup> The position of silicon necessary for this line is higher than shown on the chart. The specific gravity of silicon is variously stated.



Group I.	Group V.	Group V.
H	As	Ta
Li	As	Nb
K	pr Di	(166 <sup>V</sup> )
Cu	(166 <sup>V</sup> )	Bi
Cu	V	N
Au	Ta	P (red)
Au	(166 <sup>V</sup> )	pr Di

Several approximate lines are not given; *e. g.*, Cr, Ta, and V. The coincidences are less perfect with the elements of Group V than with all other elements.

Group II.	Group II.	Group III.
Be	(154.5 <sup>II</sup> )	VIII <sup>III</sup>
Ca	(154.5 <sup>II</sup> )	Tl
Same line {	Be	In
	Be	VIII <sup>III</sup>
	Hg	Ga
Group II.	Group II.	Group II.
Cd	Ba	VII <sup>II</sup>
Be	Zn	Cd
Mg	(171.3 <sup>II</sup> )	Hg
Group II.	Group V.	Group IV.
Be	As	Ce
Be	V	Sn
Mg	As	(175.6 <sup>IV</sup> )
Mg	(166 <sup>V</sup> )	Pb
Hg	(166 <sup>V</sup> )	Zr
Same line {	Hg	<sup>1</sup> Si
	Hg	<sup>1</sup> Si
	(171.3 <sup>II</sup> )	<sup>1</sup> Si
	(171.3 <sup>II</sup> )	<sup>1</sup> Si
	(154.5 <sup>II</sup> )	<sup>1</sup> Si
Group II.	Group VI.	Group IV.
Same line {	Mo	Th
	Mo	VIII <sup>IV</sup>
Same line {	Mo	(161.3 <sup>IV</sup> )
	Mo	C
Be	(212 <sup>VI</sup> )	(161.3 <sup>IV</sup> )
Same line {	Cr	Pb
	(167 <sup>VI</sup> )	Pb
	Mo	Pb
Same line {	O	VIII <sup>IV</sup>
	Se	VIII <sup>IV</sup>
Ca	(212 <sup>VI</sup> )	Th
Ca	ne Di	Pb

<sup>1</sup> See previous note on position of silicon.

Group II.			Group VI.			Group IV.		
	Zn, Ti, S, Ca			Te			(161.3 <sup>IV</sup> )	
	Be, Ge, Te, Ca			(167 <sup>VI</sup> )			Zr	
	Sr			W			Ce	
	Sr			W			(175.6 <sup>IV</sup> )	
	Hg			(167 <sup>VI</sup> )			Sn	
	Hg			Te			(161.3 <sup>IV</sup> )	
	Zn			U			(175.6 <sup>IV</sup> )	
Same line {	Zn	VIII <sup>II</sup>		Cr			Sn	
				Cr			Sn	
Approx.	Cd			U			Ti	
Same line {	Cd			O			<sup>1</sup> Ge	
	Cd			O			Ti	
	Cd			Cr			(161.3 <sup>IV</sup> )	
Same line {	VIII <sup>II</sup>			Se			Si	
	VIII <sup>II</sup>			Se			Ti	
	VIII <sup>II</sup>			Cr			Sn	
Approx.	VIII <sup>II</sup>			S			Zr	
Group II.			Group IV.			Group IV.		
	Be			Th			VIII <sup>IV</sup>	
Same line {	Mg			Sn			Pb	
	Mg			Sn			(161.3 <sup>IV</sup> )	
	Mg			Ge			175.6	
	Ca			Ce			Pb	
	Ba			Ti			C	
	Sr			Ce			(175.6 <sup>IV</sup> )	
	Cd			Ge			(175.6 <sup>IV</sup> )	
	Cd			Th			VIII <sup>IV</sup>	
Same line {	Hg	(171.3 <sup>II</sup> )		Ge			Si	
				Ge			Si	
Approx.	Hg			Ge			Ti	
	(171.3 <sup>II</sup> )			Ge			Ti	
	Hg			(161.3 <sup>IV</sup> )			Zr	
	VIII <sup>II</sup>			Ce			Ge	
	VII <sup>II</sup>			Zr			Ti	
	(171.3 <sup>II</sup> )			Pb			Th	
Group II.			Group VI.			Group VI.		
	Ba			S			O	
	Ba			Se			Cr	
	Ca			Te			U	
	Sr			167 <sup>VI</sup>			W	
	(171.3 <sup>II</sup> )			Se			U	
	Cd			S			W	
Approx.	Be			Cr			Mo	
Approx. only.	Mg			Se			ne Di	
	Mg			Te			ne Di	

<sup>1</sup> Point a little high.

	Group II.	Group VI.	Group III.
	171.3 <sup>II</sup>	Te	Yt
	171.3 <sup>II</sup>	Se	Sc
	171.3 <sup>II</sup>	S	In
	Group IV.	Group V.	Group V.
Same line	{ C	V	As
	{ C	V	pr Di
Same line	{ Ti	As	Nb
	{ Zr	Sb	Ta
	{ Ge	P	Ta
	{ Si	As	Nb
	<sup>1</sup> Sn	P	(166 <sup>V</sup> )
	Pb	Sb	N
Same line	{ Ge	(166 <sup>V</sup> )	VII <sup>V</sup>
	{ Si	(166 <sup>V</sup> )	VII <sup>V</sup>
	Ce	<sup>2</sup> Sb	Nb
	Pb	<sup>3</sup> Sb	N
	(VIII <sup>IV</sup> )	Bi	As
	VIII <sup>IV</sup>	(166 <sup>V</sup> )	V
Approx.	(161.3 <sup>IV</sup> )	(166 <sup>V</sup> )	Sb
	(175.6 <sup>IV</sup> )	Nb	P
	Group I.	Group VII.	Group I.
	Na	Cl	VII <sup>I</sup>
	Li	99 <sup>VII</sup>	Cr
	Li	(151.7 <sup>I</sup> )	(214.8 <sup>VII</sup> )
	K	I	Au
	K	(147.5 <sup>VII</sup> )	(169.4 <sup>I</sup> )
	Cu	Mn	Au
Approx.	Li	(186.7 <sup>VII</sup> )	Ag
Approx.	Cu	168.8 <sup>VII</sup>	Ag
	Cu	F?	Na
	Cu	(186.7 <sup>VII</sup> )	Cr
	Rb	(186.7 <sup>VII</sup> )	(169.4 <sup>I</sup> )
	Cr	F?	(169.4 <sup>I</sup> )
	Au	I	(151.7 <sup>I</sup> )
	Cr	B	(151.7 <sup>I</sup> )

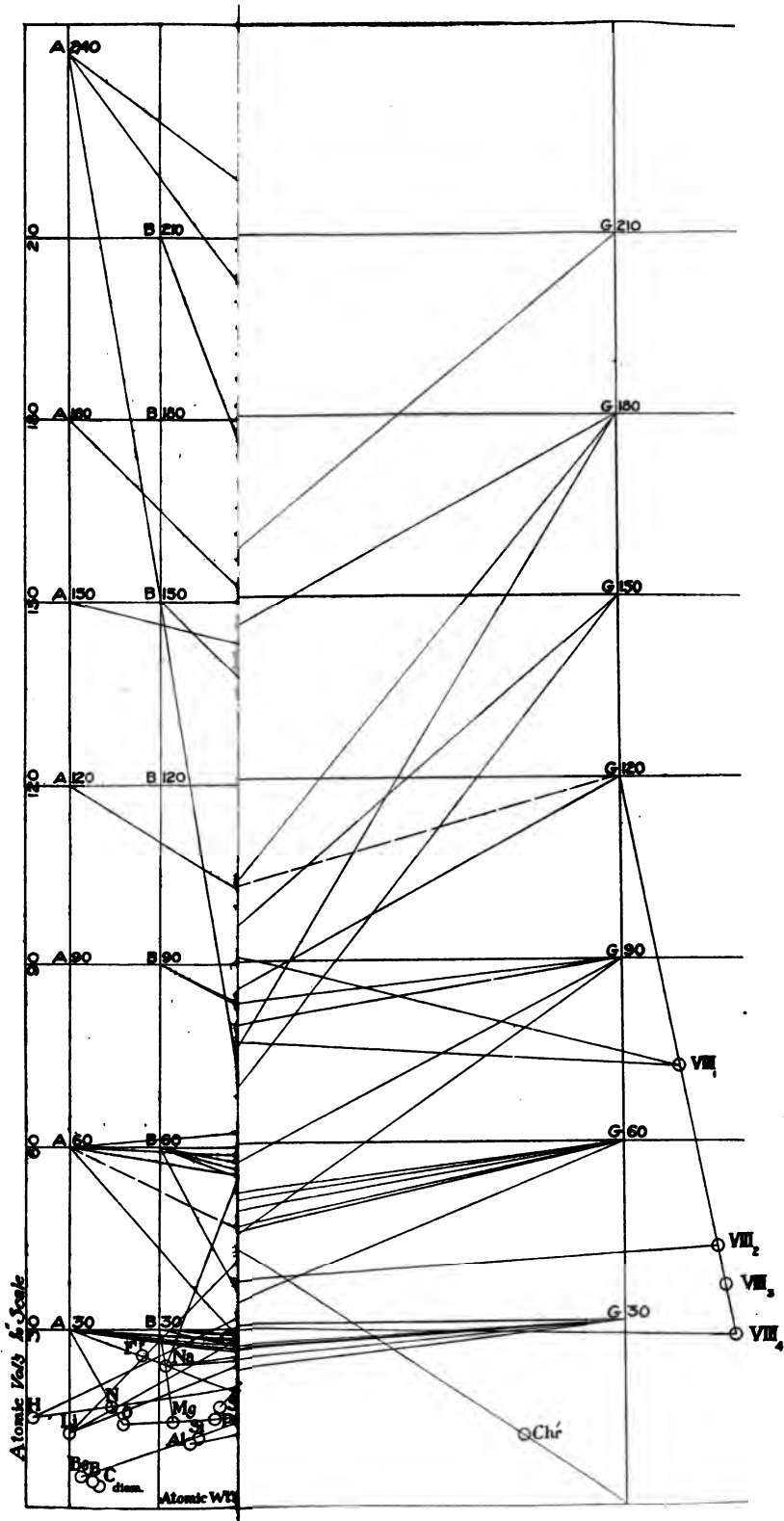
LIST OF ELEMENTS WITH SPECIFIC GRAVITIES AND ATOMIC WEIGHTS  
USED IN PREPARATION OF CHART OF ATOMIC VOLUMES.

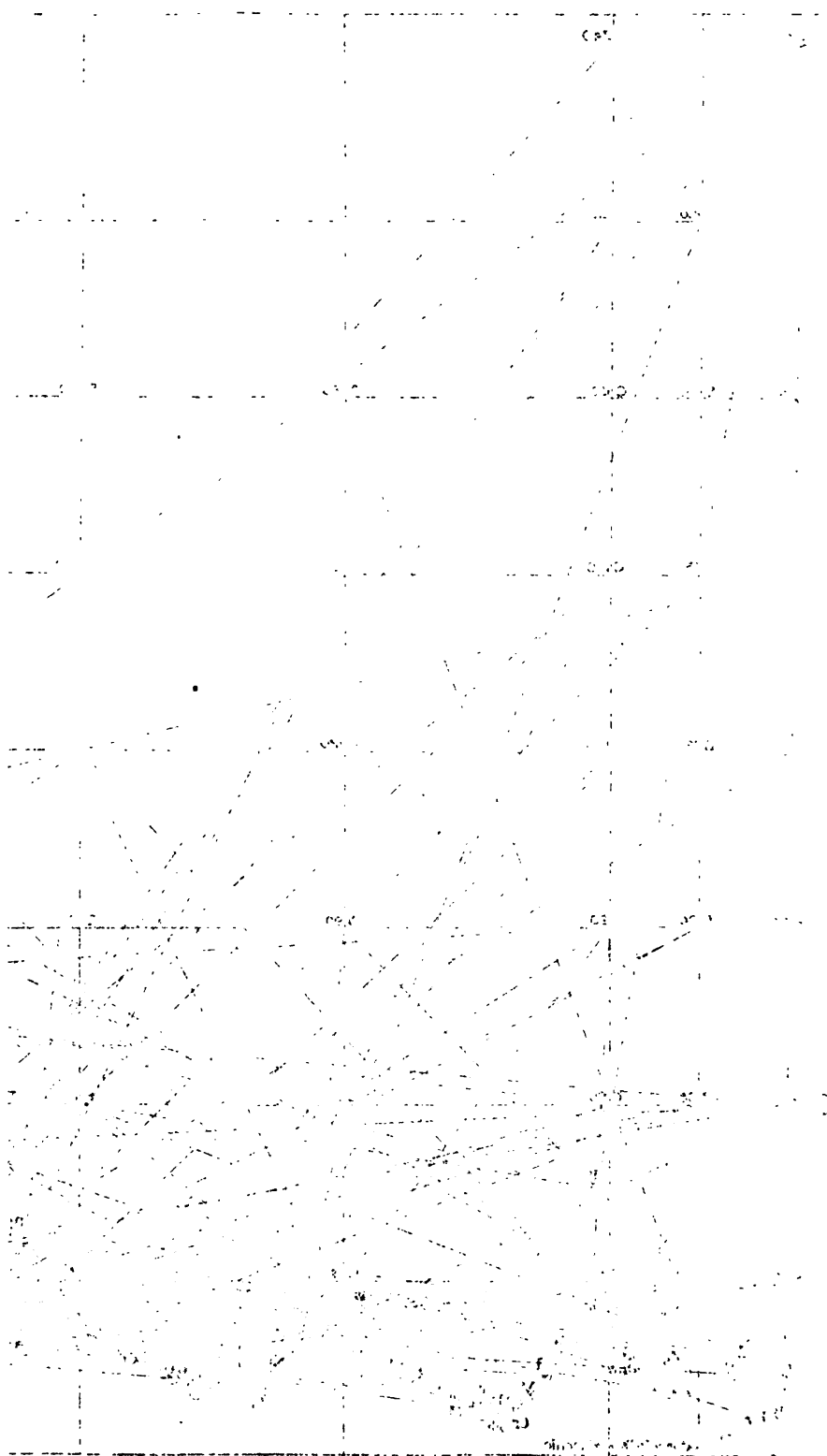
Element.	Atomic weight.	Atomic volume.	D.
Aluminum .....	27.02	10.4	2.583
Antimony .....	120.0	17.9	6.697
Arsenic .....	74.9	13.1	5.725
Barium .....	136.8	(36.5)	(3.74)
Beryllium .....	9.08	4.9	1.85

<sup>1</sup> This and several other lines point to a slightly lower atomic volume for Sn.

<sup>2</sup> This and several other lines point to a slightly lower atomic volume for Sb.

Element.	Atomic weight.	Atomic volume.	D.
Bismuth .....	208.0	20.8	10.00
Boron .....	10.97	4.1	2.68
Bromine .....	79.75	25.0	3.188
Cadmium .....	111.7	13.08	8.546
Cadmium .....	111.7	12.91	8.65
Caesium .....	132.7	70.6	1.88
Calcium .....	39.91	(c 25.3)	(1.557)
Carbon (dia.) .....	11.97	3.4	3.518
Cerium .....	139.9	20.8	6.73
Chlorine .....	35.37	26.6	1.33
Chromium .....	52.45	7.71	6.8
Cobalt .....	58.8	....	....
Copper .....	63.2	7.06	8.945
<i>n</i> -Didymium .....	....	....	....
<i>pr</i> -Didymium .....	....	....	....
Fluorine .....	....	....	....
Gallium .....	69.9	11.7	5.96
Germanium .....	72.32	13.2	5.469
Gold .....	196.7	10.2	19.3
Hydrogen .....	....	....	....
Indium .....	113.4	15.3	7.42
Iodine .....	126.53	25.8	4.917
Iridium .....	192.5	8.6	22.42
Iron .....	55.9	....	....
Lanthanum .....	138.2	22.4	6.163
Lead .....	206.4	18.2	11.35
Lithium .....	7.01	11.9	5.89
Magnesium .....	24.0	14.0	1.71
Manganese .....	55.0	6.86	8.01
Mercury .....	199.8	14.7	13.596
Molybdenum .....	95.9	11.1	8.64
Nickel .....	58.6	6.5	8.97
Niobium .....	94.0	13.3	7.06
Nitrogen .....	....	....	....
Osmium .....	190.3	8.5	22.447
Oxygen .....	15.96	....	....
Phosphorus (red) .....	30.96	14.7	2.106
Platinum .....	194.3	9.0	21.5
Potassium .....	39.04	45.1	8.65
Rhodium .....	102.7	8.48	12.1
Rubidium .....	85.2	56.0	1.52
Ruthenium .....	101.4	8.03	12.63
Scandium .....	....	....	....
Selenium .....	78.8	16.7	4.7
Silicon .....	28.3	11.4	2.49





Element.	Atomic weight.	Atomic volume.	D.
Silver.....	107.66	10.18	10.57
Sodium.....	22.995	23.3	0.985
Strontium.....	87.3	35.0	2.5
Sulphur.....	31.98	16.4	1.958
Tantalum.....	c 182.0	....	....
Tellurium.....	c 125.0	20.0	6.255
Thallium.....	203.64	....	11.81
Thallium.....	203.64	....	11.91
Thorium.....	232.0	20.9	11.1
Tin.....	118.8	16.3	7.3
Titanium.....	47.9	13.3	3.59
Tungsten.....	183.6	9.6	19.13
Uranium.....	239.0	12.8	18.685
Vanadium.....	51.2	9.3	5.5
Zinc.....	65.3	9.4	6.9
Zirconium.....	90.0	21.2	4.25

## REMARKS ON LIST OF ELEMENTS.

*Barium*.—The lines cross at an atomic volume of 36.5, equal to 3.74 specific gravity. This is between the values recorded for the element, which vary from 3.5 to 4 (mean 3.75).

*Bismuth*.—The specific gravity of liquid bismuth at the melting-point is taken; this is the highest specific gravity of the element.<sup>1</sup>

*Calcium*.—The point taken in the chart was found by the crossing of the lines. It corresponds to an atomic volume of 25.3, equal to 1.577 specific gravity. Matthiessen gives 1.57, and this apparently is the only published result.

*Germanium*.—The point taken is c 15.34, which is a little too high. 15.3 would be better, and this corresponds to a specific gravity of 5.44. Winkler gives 5.469.

*Hydrogen*.—An atomic volume of 14.6 is assigned in the chart. This is about two-tenths higher than the figure recently given by Dewar. The lines drawn through this element place it in atom-analogy with Group I. It is sometimes placed in Group VII.

*Silicon*.—The lines indicate an atomic volume of 12.5, equal to 2.26 specific gravity. This value is between the values given by Wöhler (2.49 at 10° C.) and Winkler (2.149–2.197).

*Strontium*.—The point at which the lines intersect is 34.5,

<sup>1</sup> Vincentini: *J. Chem. Soc.*, 1891, II, 518.

equal to 2.53 specific gravity. The determinations made with doubtfully pure specimens vary from 2.4 to 2.58.

*Sulphur*.—Deville's results for monoclinic sulphur.

*Thallium*.—The chart indicates a somewhat higher gravity (11.98) than Crookes obtained from the metal in the form of wire (11.91).

*Zirconium*.—The atomic volume apparently should be a little greater than 21.2.

### THE OIL OF CORN.<sup>1</sup>

By C. G. HOPKINS.

Received September 22, 1898.

THE presence of oil in the corn kernel was discovered by Bizio<sup>2</sup> in 1823. A partial analysis by Hoppe-Seyler<sup>3</sup> gave the following as the percentage composition<sup>4</sup> of the oil :

Cholesterol.....	2.65
Protogon.....	3.95
Saponifiable fats, etc.....	93.40

The statement is made that the oil contains stearin, palmitin, and much olein, and the melting-point of the fatty acids is given as 51° to 54° F. (11° to 12° C.).

Some of the so-called physical and chemical "constants," which have been determined by several investigators are given below :

	Specific gravity of oil at 15° C.	Unsaponifiable substance. Per cent.	Iodine absorption. Per cent.
Spüller <sup>5</sup> .....	.....	1.35	119.7
Smith <sup>6</sup> .....	0.9244	....	122.9
Hart <sup>7</sup> .....	0.9239	1.55	117.0
Rokitianski <sup>8</sup> .....	0.8360	....	75.8

<sup>1</sup> From advance sheets of the author's thesis "The Chemistry of the Corn Kernel," for the degree of Doctor of Philosophy, Cornell University, 1898, which will be published as Bulletin No. 53 of the University of Illinois Agricultural Experiment Station.

<sup>2</sup> *J. Chem. u. Phys.*, 1823, 37, 377.

<sup>3</sup> *Med. Chem. Untersuchungen*, 1, 162; *Bull. Soc. Chim.*, 1866, [2], 6, 342; *Jsb. Fortschritte der Chem.*, 1866, 698.

<sup>4</sup> I have not been able to see Hoppe-Seyler's original paper. Presumably the protogon is the substance now termed lecithin, and the methods employed in estimating it and cholesterol were similar to those which are discussed herein.

<sup>5</sup> Dingler's *poly. J.*, 1887, 264, 626.

<sup>6</sup> *J. Soc. Chem. Ind.*, 1892, 11, 504.

<sup>7</sup> *Ibid.*, 1894, 13, 257, from *Chem. Ztg.*, 17, 1522.

<sup>8</sup> Inaugural Dissertation, St. Petersburg, 1894; *Pharm. Ztschr. Russland*, 1895, 33, 712; *Chem. Centrbl.*, 1895, [4], 7, 1, 22.



The oil used by Spüller was the ordinary ether extract. Rokitiński used a petroleum ether extract. Hart worked with a "dark brown" sample presumably found on the market. Smith's material was obtained on the market, but was of a "bright golden color" and was probably a fair sample of corn oil.

Spüller observed that the oil absorbed no oxygen from the air even after fourteen days' exposure. Smith states that the freezing-point of the oil is below  $-20^{\circ}$ . Hart gives the melting-point of the fatty acids as  $25^{\circ}$ . Rokitiński reports further qualitative chemical work which showed the oil to contain oleic and linolic acids. It is evident from the specific gravity and the iodine absorption that the material with which he worked was not ordinary corn oil.

Wiley and Bigelow<sup>1</sup> have recently found the heat of combustion of oil of corn to be 9280 calories per gram.

#### EXPERIMENTAL.

In a preliminary study a small amount of oil was obtained by collecting the ether extract from a large number of proximate analyses of corn. In this, advantage was taken of the fact that the oil is moderately soluble in alcohol when hot and but slightly so at ordinary temperatures.<sup>2</sup>

The oil was transferred from the small flasks, used in its extraction, by means of hot alcohol to a single vessel. On cooling the oil precipitated and settled to the bottom, the alcohol being each time decanted from the collected oil, and used in transferring the next lot. Finally the alcohol was evaporated, and the oil dried to constant weight in a water oven. When freshly obtained from white dent corn the oil is nearly colorless, but on standing a pale yellow and finally a deep golden color develops, plainly indicating a gradual change in its condition, presumably due to absorption of oxygen. This was confirmed by determining the iodine absorption which was found to be 115.5 per cent.

A large quantity of corn oil, including samples from four different sources,<sup>3</sup> was then secured in order to make a more

<sup>1</sup> This Journal, 20, 309.

<sup>2</sup> Smith has found the solubility of corn oil in alcohol by volume to be two per cent. at  $16^{\circ}$  and thirteen per cent. at  $63^{\circ}$ .

<sup>3</sup> Samples of corn oil were very kindly furnished me by President Wm. F. Piel, Jr., of The National Starch Manufacturing Company, New York City; by The Chas. Pope Glucose Company, Geneva, Ill.; by The Glucose Sugar Refining Company, Chicago; and by Messrs. Elbert and Gardner, New York City.

thorough investigation. The oil is obtained as a by-product in the manufacture of corn-starch and glucose-sugar, and all of the samples secured were of a pale straw color and evidently fresh and pure.

#### SPECIFIC GRAVITY.

Three of these samples of corn oil were sufficient in quantity to enable me to make determinations of their specific gravity by means of a delicate Westphal balance which by trial gave the specific gravity of pure water at 15° as 1.000°. The samples of oil gave the following results :

	I.	II.	III.
Specific gravity at 15°.....	0.9245	0.9262	0.9258

#### MELTING-POINT.

Preliminary experiments confirmed the observation of Smith that the oil is still fluid at  $-20^{\circ}$ , a temperature of  $-23^{\circ}$  (obtained with snow and concentrated sulphuric acid) failing to solidify the oil. It was found, however, that the oil became hard and solid at about  $-36^{\circ}$ .

The melting-point was determined by a modification of the method of the Association of Official Agricultural Chemists.<sup>1</sup>

In a tall beaker of about two and five-tenths liters' capacity was placed a small quantity of concentrated sulphuric acid (to absorb water vapor so that the apparatus would remain transparent at low temperatures). A second beaker of about two liters' capacity was placed in the first, being supported by the rim without touching the bottom. A one-liter beaker taller than the second was placed in the latter and filled with alcohol, the space between the two being filled with solid carbon dioxide. A glass tube thirty mm. in diameter and closed at the bottom was fitted into the inner beaker with a large cork, the tube being about one-third filled with a mixture of one volume of concentrated sulphuric acid and three volumes of absolute alcohol, and then nearly completely filled with absolute alcohol. The temperature of the alcohol in the beaker was kept uniform throughout by constant stirring with a wire which passed through the cork and terminated in a ring surrounding the glass tube. A heavy glass spoon and a glass spatula were placed in the alcohol.

<sup>1</sup> U. S. Dept. of Agr., Div. of Chem., Bull. 46, 34.

When the temperature reached  $-50^{\circ}$ , the spoon was removed and a drop of the oil at once let fall upon it. A thin, solid, white, opaque disk formed, and was quickly made to drop into the inner tube by using the glass spatula. The disk of solidified oil settled through the absolute alcohol to the denser liquid below and there remained in suspension.

The beaker which had contained carbon dioxide was replaced by another and the temperature allowed to slowly rise. An alcohol thermometer was used for reading the temperatures below the freezing-point of mercury. Above  $-38^{\circ}$  a delicate mercury thermometer was employed.

As the temperature rose the disk remained unchanged until at  $-19^{\circ}$  it began to lose its opacity. At  $-14^{\circ}$  it had become perfectly transparent, but no change in shape could be detected below  $-7^{\circ}$ . The disk was much contracted and thickened at  $-5^{\circ}$  and became entirely symmetrical in form at  $-2.3^{\circ}$ . A second determination gave practically the same results, the final reading being  $-2.4^{\circ}$ . The change in temperature (when near the melting-point) required five to six minutes for one degré.

To determine the change in the consistency of the oil, a thin-wall tube of eight mm. diameter, closed at the bottom and containing one cm. of the oil, was placed in alcohol at  $-45^{\circ}$ . After the oil had become solid a glass rod twenty cm. long and two mm. thick (the lower end being widened to five mm. diameter), was placed in the tube so that its weight was entirely supported by the solidified oil. At  $-13^{\circ}$  the oil had become transparent but still supported the rod. At  $-10^{\circ}$  the rod began to settle appreciably and at  $-9^{\circ}$  it had passed through the centimeter of oil to the bottom, although a disk of oil suspended beside the tube in the same liquid had not changed appreciably in shape. The change of temperature from  $-10^{\circ}$  to  $-9^{\circ}$  required five minutes.

#### IODINE ABSORPTION.

The method of Hübl<sup>1</sup> was employed for this determination, except for certain details of the process.

Standard sodium thiosulphate solution was prepared by dissolving 47.2 grams of the crystallized salt ( $\text{Na}_2\text{S}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$ ) in water and diluting to two liters. From theory one cc. of this

<sup>1</sup> *J. Soc. Chem. Ind.*, 1884, 3, 641.

solution should be equivalent to 12.06 milligrams of iodine if the salt were pure.<sup>1</sup> The solution was standardized with resublimed iodine with the following results :

Iodine taken .....	0.5160	0.5574 gram.
Thiosulphate solution required ....	42.9	46.4 cc.
Iodine equivalent to one cc .....	12.03	12.01 milligrams.

The average of these results, 12.02, was used in the following work :

The iodine solution, containing fifty grams iodine, and sixty grams mercuric chloride in two liters of alcohol, was standardized whenever used.

Little pipettes of about five-tenths cc. capacity were placed in five cc. vials nearly filled with the corn oil, the bulb of the pipette being immersed, and the whole weighed. The measure of oil was then transferred to a 500 cc. glass-stoppered bottle, the pipette returned to the vial, and the exact weight of oil taken determined by difference. The duplicate is taken immediately and necessitates only one more weighing. Ten cc. of chloroform and forty cc. of iodine solution were added to the oil. After two hours twenty-five cc. of ten per cent. potassium iodide solution and about 125 cc. of water were added and the excess of iodine determined by titrating with the sodium thiosulphate solution, starch indicator being added near the close of the reaction.

Duplicate determinations of four different samples of oil from as many different sources gave the following results :

	Oil taken. Gram.	Iodine absorbed. Gram.	Iodine absorbed. Per cent.
1.....	{ 0.3473 0.3844	0.4255 0.4729	122.5 123.0
2.....	{ 0.4251 0.4714	0.5179 0.5729	121.8 121.5
3.....	{ 0.4281 0.4742	0.5212 0.5772	121.7 121.7
4.....	{ 0.4326 0.5168	0.5324 0.6351	123.1 122.9

#### OXYGEN ABSORPTION.

In order to afford a large surface for the absorption of oxygen, the oil was placed in a large crystallizing dish of seventy-five

<sup>1</sup> Sutton's Volumetric Analysis, 1890, 115, states that standard sodium thiosulphate solution may be made by simply dissolving an exact weight of the crystallized salt,  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , in water and diluting to a definite volume.

mm. diameter. This was allowed to stand at the room temperature, the weight of the oil being determined from time to time as follows :

	Grams.
Weight of oil taken .....	2.1732
Weight after 1 day .....	2.1722
"    "    7 days.....	2.1718
"    "   11 days .....	2.1718
"    "   12 "    .....	2.1718

These results confirm those of Spüller, showing that the oil does not take up oxygen under these conditions.

The dish was then placed in a water-oven and the following data<sup>1</sup> obtained :

	Grams.
Weight after 1 hour .....	2.1726
"    "    1 day .....	2.1996
"    "    2 days .....	2.2488
"    "    3 "    .....	2.2590
"    "    4 "    .....	2.2588
"    "    5 "    .....	2.2558
"    "    6 "    .....	2.2513
"    "    7 "    .....	2.2448

The first action of air upon the hot oil is evidently the direct addition of oxygen ; but after two or three days the oil began to turn noticeably darker in color and finally to lose weight, evidently due to a secondary reaction which effects some decomposition of the oil with formation of volatile products.

#### LECITHIN.<sup>2</sup>

A weighed quantity of oil was mixed with potassium nitrate and sodium carbonate in a platinum dish and ignited until the carbon was completely burned. The fused mass was dissolved in dilute hydrochloric acid, and the total phosphoric acid determined.<sup>3</sup> The amount of lecithin was calculated by multiplying the weight of magnesium pyrophosphate obtained by the factor

<sup>1</sup> These results emphasize the importance of avoiding the presence of oxygen in drying corn or corn oil in analytical work.

<sup>2</sup> Lecithin is commonly regarded as a compound of the base, neurine, with distearyl-glycerophosphoric acid, although one or both of the stearic acid radicals may be replaced by radicals of palmitic or oleic acid, and the neurine (trimethylhydroxyethyl ammonium hydroxide) is sometimes replaced by another base ; e. g., betaine.

<sup>3</sup> Cf. Hoppe-Seyler, *Jsb. Fortschritte der Chem.*, 1866, 744 ; Schulze and Frankfurt, *Landwirtschaftliche Versuchs-Stationen*, 1893, 43, 207.

7.25.<sup>1</sup> Duplicate determinations gave the following results:

	Grams.	Grams.
Oil taken.....	10.728	6.435
KNO <sub>3</sub> used <sup>2</sup> .....	10.0	35.0
Mg <sub>3</sub> P <sub>2</sub> O <sub>8</sub> obtained.....	0.0221	0.0132
Lecithin.....	0.1602	0.0957
	Per cent.	Per cent.
Lecithin in oil <sup>3</sup> .....	1.49	1.49

#### CHOLESTEROL.<sup>4</sup>

To determine cholesterol<sup>5</sup> about fifty grams of the oil were saponified on the water-bath with twenty grams of potassium hydroxide and 100 cc. of seventy per cent. alcohol. The soap was transferred to a large separatory funnel with 200 cc. of water and shaken first with 500 cc. of ether and then three times with 250 cc. of ether. The four portions of separated ether were combined, and the ether distilled, the residue being resaponified with two grams of potassium hydroxide and ten cc. of seventy per cent. alcohol. The solution was then transferred to a small separatory funnel with twenty cc. of water and shaken with 100 cc. of ether. After separating the aqueous layer the ether solution was washed four times with ten cc. of water, the ether solution being finally transferred to a weighed flask, the ether distilled and the weight of the dry residue (cholesterol) determined. Three determinations gave the following results:

	Grams.	Grams.	Grams.
Oil taken .....	50.16	53.50	54.24
Cholesterol obtained..	0.7002	0.7114	0.7512
	Per cent. <sup>6</sup>	Per cent.	Per cent.
Cholesterol in oil .....	1.40	1.33	1.38

The cholesterol was recrystallized from absolute alcohol in characteristic glistening plates, melting at 137° to 137.5°. It also gave the characteristic color reactions<sup>7</sup> for cholesterol: (1)

<sup>1</sup> 7.25 parts of lecithin (C<sub>44</sub>H<sub>88</sub>O<sub>8</sub>PN) yield one part of magnesium pyrophosphate.

<sup>2</sup> The proportions of potassium nitrate used were purposely varied, but the results indicate that the smaller proportion was sufficient.

<sup>3</sup> By extracting corn with ether and alcohol, successively, Schulze and Frankfurt (reference above) have obtained amounts of phosphoric acid equivalent to 0.25 to 0.26 per cent. of lecithin in the corn.

<sup>4</sup> A monatomic alcohol, C<sub>26</sub>H<sub>44</sub>OH.

<sup>5</sup> Cf. Bömer, *Ztschr. für Untersuchung der Nahrungs- und Genussmittel*, 1898, 21, for recent work on the details of this method.

<sup>6</sup> Spüller had obtained 1.35 per cent. and Hart 1.55 per cent. of unsaponifiable matter.

<sup>7</sup> Watts' Dictionary, 1889, 2, 147.

when shaken with chloroform and sulphuric acid; (2) when evaporated to dryness with nitric acid; (3) when warmed with hydrochloric acid and ferric chloride.

## TOTAL FATTY ACIDS.

After removing the cholesterol from about fifty grams of oil the remaining soap solution (about 500 cc.) was acidified with hydrochloric acid and shaken in a separatory funnel. An ethereal layer of about 150 cc. at once separated. After adding 100 cc. more ether and thoroughly shaking, the aqueous layer was drawn off, the ether solution of the fatty acids washed with several portions of water and then transferred to a weighed flask, the ether distilled off, a few cubic centimeters of absolute alcohol dissolved in the residue and evaporated to remove traces of water, and the weight of the total fatty acids determined:

	Grams.
Oil taken .....	50.160
Fatty acids obtained.....	46.935
	Per cent.
Fatty acids in oil .....	93.57

The fatty acids form a solid mass at 15°, but melt nearly completely at one or two degrees above, the last particles of solid disappearing at 23°. Prepared as described the fatty acids absorbed only 126.4 per cent. of iodine instead of 130.7 per cent. as calculated from the iodine absorption of the oil. This indicates that oxygen had been absorbed by the acids during the process of separation. It was found that oxygen is slowly absorbed by the fatty acids while standing in a desiccator at the ordinary temperature. At 100° the absorption is much more rapid although, as with the oil, secondary reactions soon begin at the higher temperature. The change in weight was found to be as follows:

Time. In days.	In desiccator. Grams.	In water-oven. Grams.
0 .....	1.9685	2.2740
1 .....	1.9692	2.3106
2 .....	1.9717	2.3366
3 .....	1.9777	2.3366
4 .....	1.9847	2.3282
8 .....	2.0231	...
12 .....	2.0665	...
16 .....	2.0911	...
22 .....	2.1157	...
28 .....	2.1293	...
34 .....	2.1297	...

All action apparently ceased after about one month's time. A considerable portion of the fatty acids had separated in the solid form and of a pure white color, while the other portion remained a colorless, oily liquid.

It is of interest to note the apparent relation between the iodine absorption and the oxygen absorption by the fatty acids. As already shown the fatty acids as prepared absorbed 126.4 per cent. of iodine. If an equivalent amount of the bivalent oxygen may be absorbed instead of the univalent iodine then eight per cent. of oxygen should be taken up. The results show that 1.9685 grams of the fatty acids absorbed 0.1612 gram of oxygen, an amount equal to eight and two-tenths per cent.

Time would not permit the preparation of the fatty acids in a manner which would prevent the absorption of oxygen during the process, and then a repetition of the quantitative determination of the absorption. This is especially desirable in order to confirm the results as given above, and the writer expects to investigate this point more fully in the future.

#### VOLATILE ACIDS.

About five grams of oil were saponified in a 500 cc. flask with two grams of potassium hydroxide and forty cc. of eighty per cent. alcohol. After evaporating the last of the alcohol, 100 cc. of recently boiled water were added, the soap solution acidified with forty cc. of dilute sulphuric acid (1:10), a few pieces of freshly ignited pumice-stone added, the flask connected with a condenser by means of a safety bulb tube, and 110 cc. of distillate collected. After mixing, 100 cc. were passed through a dry filter and titrated with one-twenty-fifth normal barium hydroxide solution.

Four determinations gave the following results :

	Grams.	Grams.	Grams.	Grams.
Oil taken.....	4.506	5.894	5.671	5.718
	cc.	cc.	cc.	cc.
N/25 barium hydroxide required..	1.3	1.5	1.4	1.3

As two blank determinations required one and three-tenths and one and five-tenths cc., respectively, of the barium hydroxide solution it is evident that the oil contains no volatile acids.<sup>1</sup>

<sup>1</sup> Spüller gives Reichert's number for the volatile acids as 0.33; Smith states that the oil examined by him contained volatile acids equivalent to 0.36 per cent. of potassium hydroxide; and Morse (New Hampshire Experiment Station Bulletin, 1892, 16, 19) gives volatile acids as three and two-tenths per cent. in a sample of corn oil which absorbed 112.8 per cent. of iodine.



## SEPARATION AND DETERMINATION OF FATTY ACIDS.

It has been found especially by Hazura<sup>1</sup> and his associates that the oxidation of unsaturated fatty acids by alkaline potassium permanganate serves as a basis for the approximate separation of several fatty acids. Under proper conditions the oxidation is chiefly confined to the direct addition of the hydroxyl group (OH) wherever "free valences" exist. The following shows the relations among several acids in the series containing eighteen atoms of carbon in the molecule :<sup>2</sup>

## Unsaturated acids.

## Saturated acids.

Stearic,  $C_{18}H_{36}O_2$ .Oleic,  $C_{18}H_{34}O_2$ , oxidizes to dihydroxy stearic,  $C_{18}H_{34}(OH)_2O_2$ .Linolic,  $C_{18}H_{32}O_2$ , oxidizes to tetrahydroxy stearic,  $C_{18}H_{32}(OH)_4O_2$ .Linolenic,  $C_{18}H_{30}O_2$ , oxidizes to hexahydroxy stearic,  $C_{18}H_{30}(OH)_6O_2$ .

After removing the cholesterol from 53.5 grams of oil, the combined soap solution was heated till the dissolved ether was distilled, cooled, and diluted to two liters. Two liters of a one and five-tenths per cent. potassium permanganate solution were then gradually added with constant stirring. After ten minutes the precipitated manganese hydroxide was filtered off, and the clear filtrate acidified with hydrochloric acid. The precipitate thus formed was filtered off, washed, air-dried, and then extracted with ether. The residue insoluble in ether weighed, after drying, eighteen grams. It was extracted with boiling water until but two grams remained, which, when again extracted with ether, left a residue of six-tenths gram and soluble in boiling water.

The substance dissolved in hot water was practically completely precipitated as the solution cooled<sup>3</sup> and proved to be sativic acid (tetrahydroxystearic acid), as is indicated by the method of formation and by its solubility in hot water. The melting-point<sup>4</sup> of the dried substance was  $157^{\circ}$ – $159^{\circ}$ .

The quantitative synthesis of the potassium salt was effected by dissolving a weighed amount of the acid in warm alcohol and titrating with standard alcoholic potassium hydroxide solution :

<sup>1</sup> *Monatsh. Chem.*, 1886 to 1889, 7 to 10.

<sup>2</sup> Cf. Hazura: *Ibid.*, 1887, 8, 269.

<sup>3</sup> 2000 cc. of the filtrate from the precipitated sativic acid required only five-tenths cc. of fifth-normal potassium hydroxide to show alkalinity with phenolphthalein.

<sup>4</sup> Bauer and Hazura, *Monatsh. Chem.*, 1886, 7, 225, give  $160^{\circ}$  as the melting-point of several samples of sativic acid, prepared in a manner similar to the above.

Sativic acid taken.	Potassium hydroxide required.	Per cent. potassium in product. <sup>1</sup>	Per cent. potassium (theory). <sup>2</sup>
1.000	0.1604	10.08	10.14

The ether solutions obtained as described above were combined and the ether distilled. The residue was solid at the room temperature, melted gradually as the temperature rose from 40° to 60°, and was found to absorb 79.2 per cent. of iodine, thus showing very incomplete oxidation of the unsaturated acids.

A second lot of corn oil (54.24 grams) was oxidized by alkaline permanganate, the cholesterol and then the dissolved ether having been previously removed. The soap was diluted to two liters and cooled to 0° by ice kept in the solution. A solution of potassium permanganate containing eighty grams in two liters of water was slowly added with constant stirring. After thirty minutes precipitated matter was filtered off and washed; the clear filtrate was acidified with 150 cc. of concentrated hydrochloric acid; the precipitated acids were filtered off, dried, and extracted with ether. The residue insoluble in ether (17.7 grams, was dissolved in boiling ninety-five per cent. alcohol. On cooling, the sativic acid separated in the crystalline form, melting at 161°–163°.

By distilling the ether from the solution obtained as above described, a brown residue (nine and five-tenths grams) was obtained which melted at 55° to 60° and showed an iodine absorption of only nine and two-tenths per cent.

The aqueous acid solution from which the insoluble organic acids had been precipitated by hydrochloric acid was evaporated nearly to dryness, a black tarry mass gradually separating, showing that, although a small amount of unsaturated acids had been unacted upon, the oxidation had gone far beyond the simple addition of hydroxyl groups to the unsaturated compounds.

To further investigate the fatty acids, a method essentially that of Muter<sup>3</sup> was tried for their separation and determination. It is based upon the fact that the lead salts of the unsaturated acids, oleic, linolic, etc., are soluble in ether; while the lead salts of the saturated acids, stearic, palmitic, etc., are not.

<sup>1</sup> Calculated weight =  $1.000 + 0.1604 \frac{39.14 - 1.008}{56.148}$

<sup>2</sup> For  $C_{18}H_{31}(OH)_2O_2K$ .

<sup>3</sup> *Analyst*, 1877, 2, 73.

About one and five-tenths grams of the oil were saponified with alcoholic potash and the soap dissolved in water, the unsaponifiable substance (cholesterol) being separated from the soap solution by shaking with ether. The solution was then neutralized with acetic acid, and the fatty acids precipitated with lead acetate, a slight excess being added. The lead salts were washed with water, and then transferred with fifty cc. of ether to a glass cylinder of about sixty cc. capacity, which was stoppered and then violently shaken for five to ten minutes. The small quantity of matter insoluble in ether was then allowed to settle. A stopper carrying two glass tubes similar to those used in the ordinary washing bottle was placed in the cylinder, the long tube reaching nearly to the undissolved sediment. By blowing in the short tube the clear solution is transferred almost completely without disturbing the sediment. The undissolved substance was then shaken with more ether, allowed to settle, and the ether transferred as before as completely as possible. This treatment was twice more repeated. The undissolved lead salt was then warmed with about twenty-five cc. of dilute hydrochloric acid, till the fatty acid separated; and, after cooling sufficiently, the whole was transferred to a 250 cc. graduated bulb tube, ether being used to complete the transfer. The portion of the tube below the bulb contained fifty cc. and was graduated to two-tenths cc. A small glass tube carrying a stopcock was sealed in just below the fifty cc. mark. The tube was filled to the 250 cc. mark (above the bulb) with ether, and thoroughly shaken. The aqueous layer, containing the excess of hydrochloric acid and the precipitated lead chloride was allowed to separate.

The volume of ether solution was observed, and 200 cc. of it were drawn off into a weighed flask, evaporated to dryness, and the weight of the residue determined.

Duplicate determinations gave the following :

	Grams.	Grams.
Oil taken .....	1.60	1.610
	cc.	cc.
Volume of ether solution .....	222.4	221.0
Ether solution taken .....	200.0	200.0
	Gram.	Gram.
Saturated acids obtained .....	0.0670	0.0648
	Per cent.	Per cent.
Saturated acid in oil .....	4.66	4.44

The residue of saturated acids formed a white solid mass. It was dissolved in hot alcohol and allowed to crystallize. The melting-point was  $57^{\circ}$ . The quantity of the saturated acids thus obtained was considered too small for further satisfactory examination (see foot-note below).

Before the lead salts of the saturated acids were completely washed by decantation<sup>1</sup> the clear ether solution of the lead salts of the unsaturated acids absorbed oxygen, and became cloudy, a white precipitate forming in considerable amount. Two samples of the atmosphere in the cylinders above the solutions were drawn off in gas burettes; and, after removing the ether vapor, the residual air was found to contain only 15.3 per cent. and 13.9 per cent., respectively, of oxygen instead of 20.8 per cent. as found in the air of the laboratory.

By subtracting the percentage (4.55) of saturated acids found in the oil from that of the total fatty acids (93.57) the amount of total unsaturated acids is found to be 89.02 per cent., consisting of oleic and linolic acids. (The melting-point of the sativic acid obtained and the composition of its potassium salt prove the absence of linusic acid in the products of oxidation, and, hence, of linolenic acid in the total fatty acids.)

From the iodine absorption, the amounts of oleic and linolic acids can be accurately determined. Thus:

Oleic acid,  $C_{18}H_{34}O_2 + I_2 = C_{18}H_{34}I_2O_2$ , diiodostearic acid.

Linolic acid,  $C_{18}H_{32}O_2 + 2I_2 = C_{18}H_{32}I_4O_2$ , tetraiodostearic acid.

As 89.02 grams of these unsaturated acids in the ratio in which they exist in corn oil absorb 122.3 grams of iodine the following equation can be stated,  $x$  being the number of grams of oleic acid:

$$x \frac{254}{282} + (89.02 - x) \frac{508}{280} = 122.3$$

The oleic acid is found to be 42.92 grams and the linolic acid 46.10 grams.

By subtracting from the amount of saturated acids the equiv-

<sup>1</sup> At least two days' time is required for this process, and even this was found more satisfactory than filtration. I have no doubt that, if centrifugal force were substituted for gravity, the washing by decantation could be done much better and so quickly that the unsaturated acids could also be determined before the absorption of any appreciable amount of oxygen. Quantities of the separated materials sufficient for further examination could doubtless be obtained in a short time. No suitable centrifugal was at hand for this work.

alent of the stearic acid contained in the lecithin, and calculating to the respective glycerol esters the remaining saturated acids (as stearic acid), the oleic acid, and the linolic acid, the following summary is obtained as the composition of the oil of corn :

	Per cent.
Cholesterol .....	1.37
Lecithin .....	1.49
Stearin (?) .....	3.66
Olein .....	44.85
Linolin .....	48.19
Total .....	99.56

### SOME ERRORS IN THE DETERMINATION OF NITROGEN.<sup>1</sup>

By C. G. HOPKINS.

Received September 22, 1898.

THE determination of nitrogen was made by the ordinary Kjeldahl method. The metallic mercury used in the digestion was measured in a capillary tube, one end of which is doubly bent so as to form a loop, the short arm of which is turned back upon itself near the end while the long arm serves as a handle. The loop is made sufficiently narrow to pass into the mercury bottle, and of sufficient length to retain, when raised above the liquid, the exact quantity of mercury required for a single determination. By blowing in the longer arm the mercury is emptied into the digestion flask.

Heavy copper flasks were used in the distillation with much satisfaction, the sodium hydroxide solution (containing the necessary amount of potassium sulphide) being added in sufficient excess to "bump" before the contents may become dry, thus serving as a signal that the distillation has gone far enough.

Two common sources of error in the nitrogen determination were found and investigated. In titrating an acid solution in an open vessel with standard ammonia solution a very appreciable error is introduced by the volatility<sup>2</sup> of the ammonia, although the only possible loss is from the tip of the-burette and from the falling drops.

<sup>1</sup> From advance sheets of the author's thesis, "The Chemistry of the Corn Kernel," for the degree of Doctor of Philosophy, Cornell University, 1898, which will be published as Bulletin No. 33 of the University of Illinois Agricultural Experiment Station.

<sup>2</sup> Rempel has already shown that dilute ammonia solution drawn into beakers or evaporating dishes and then titrated suffers marked loss.—*Ztschr. angew. Chem.*, 1889, 331.

In the following work ammonia of about one-sixth normal strength was used, the hydrochloric acid being of such strength that three cc. were equivalent to approximately four cc. of ammonia. The hydrochloric acid was measured from an automatic overflow pipette of fifteen cc. capacity, and the ammonia from an automatic overflow burette graduated to 0.05 cc. and drawn to a fine tip at the outlet. The pipette and burette were each provided with three-way stop-cocks through which the standard solutions were drawn from the stock bottles by means of siphons. Perfectly neutral water free from ammonia and carbon dioxide was used for diluting. Lacmoid served as the indicator and gave an exceedingly sharp end-reaction.

By titrating in beaker flasks with the tip of the ammonia burette well below the top of the flask the following results were obtained, the length of time taken in making the titration being also given :

No.	Hydrochloric acid taken. cc.	Ammonia required. cc.	Time, minutes.
1.....	15	20.10	1
2.....	15	20.08	1
3.....	15	20.12	1
4.....	15	20.30	2
5.....	15	20.25	2
6.....	15	20.40	3

By titrating in an Erlenmeyer flask attached to the burette by means of a rubber stopper,<sup>1</sup> provided with a capillary tube for relieving the pressure, the following results were obtained :

No.	Hydrochloric acid taken. cc.	Ammonia required. cc.	Time, minutes.
1.....	15	19.82	1
2.....	15	19.83	1
3.....	15	19.81	3
4.....	15	19.81	5

As from three to five minutes are taken to make a titration when the amount of ammonia required is not known, as in ordinary nitrogen determinations, the error<sup>2</sup> from titrating in open vessels becomes an important factor, the total variation in the two series of experiments above noted amounting to six-tenths

<sup>1</sup> By using a stopper which has been bored nearly through from the small end by a large borer, the flask may easily be given a free rotary motion.

<sup>2</sup> Confirmed by recent (unpublished) work of Dr. F. L. Kortright, of Cornell University.

cc. or three per cent. of the ammonia required. The fact that the density of ammonia gas is but little more than half that of air explains its rapid upward diffusion from an open vessel.

Another error in nitrogen determinations may occur in the distillation by loss of ammonia from the receiving flask in case there is not sufficient acid *above the end of the delivery-tube* to neutralize all of the ammonia distilled over.

In the following work a quantity of a very dilute solution of ammonium chloride was prepared by exactly neutralizing standard hydrochloric acid with standard ammonia and diluting with ammonia-free water. A quantity of this solution equivalent to twelve cc. of standard ammonia was placed in a distillation flask with an excess of sodium hydroxide and distilled into fifteen cc. of standard hydrochloric acid diluted to about forty cc., the end of the delivery-tube from the condenser dipping *well into the acid solution*. The relation of the standard acid and ammonia solutions was such that fifteen cc. hydrochloric acid were equivalent to 19.82 cc. ammonia. Six distillations were made, in each case ammonium chloride equivalent to twelve cc. of standard ammonia solution being taken. Following are the amounts of standard ammonia solution required to neutralize the excess of acid :

No.	Required. cc.	Calculated. cc.	Error. cc.
1.....	8.20	7.82	0.38
2.....	7.85	7.82	0.03
3.....	7.93	7.82	0.11
4.....	8.60	7.82	0.78
5.....	7.84	7.82	0.02
6.....	7.95	7.82	0.13

Two of these are practically exact, the other four showing errors varying from 0.11 cc. to 0.78 cc. of standard ammonia.

This work was repeated with the distillation from quantities of ammonium chloride equivalent to fifteen cc. of standard ammonia solution, the other conditions being as before. Following are the amounts of standard ammonia solution required to neutralize the excess of acid :

No.	Required. cc.	Calculated. cc.	Error. cc.
1 .....	6.10	4.82	1.28
2 .....	5.40	4.82	0.58
3 .....	5.95	4.82	1.13
4 .....	6.20	4.82	1.38
5 .....	5.65	4.82	0.83
6 .....	5.18	4.82	0.36

. Diluting the residues in the distillation flasks with ammonia-free water, and distilling, gave no further addition of ammonia in any case.

It was observed that in both trials the greatest errors occurred with Nos. 1 and 4. A careful inspection of the apparatus showed all connections to be perfect. It was observed, however, that the delivery-tubes from Nos. 1 and 4 did not reach as far into the acid solution as most of the others.

With the thought that possibly ammonia escaped from the receiving-flasks, the following six distillations were made, in each the quantity of ammonium chloride employed being equivalent to 19.32 cc. of standard ammonia solution; thus, exactly five-tenths cc. of standard ammonia should have been required to neutralize the excess of acid. Some lacmoid indicator was added to the acid solutions in receiving-flasks Nos. 1, 3, and 5; strips of moistened red litmus paper were also hung in the necks of these flasks. During the process of distillation, receiving-flasks 2, 4, and 6 were agitated to keep their contents thoroughly mixed.

It was observed that, during the process of distillation, in receiving-flasks 1, 3, and 5 the liquid above the end of the delivery-tube turned blue, while a layer of liquid below this remained red; also that the moistened red litmus paper hung in the necks of these flasks turned blue.

In titrating the excess of acid the amounts of standard ammonia required were as follows:

No.	Required. cc.	Calculated. cc.	Error. cc.
1 .....	2.60	0.50	2.10
2 .....	0.50	0.50	0.00
3 .....	2.27	0.50	1.77
4 .....	0.53	0.50	0.03
5 .....	1.99	0.50	1.49
6 .....	0.50	0.50	0.00



The explanation for the separation of the liquid in the receiving-flasks into two layers as described is to be found in the different densities of aqueous solutions of ammonia and hydrochloric acid.

In subsequent work I have used delivery-tubes reaching to the very bottom of the receiving flasks, and contracted at the end to an aperture of but four or five mm. diameter. This insures considerable agitation of the contents of the receiving flask produced by irregularities in the boiling of the liquid in the distillation flask.

This loss of ammonia shown to have taken place from the very dilute solution in the receiving flask after cooling by an efficient condenser emphasizes the results of the preceding work on titration and the importance of avoiding a common error in that process.

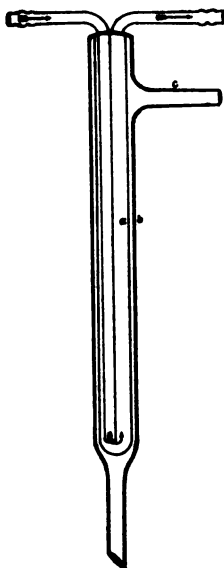
### A CONDENSER FOR EXTRACTION WORK.<sup>1</sup>

By C. G. HOPKINS.

Received September 22, 1898.

MAINLY to avoid the constant trouble of having atmospheric moisture condense upon the outer surface of a Liebig or Allihn condenser and run down over the extraction apparatus, the following form of condenser was designed :

This condenser is made entirely of glass, and consists of a *thin* glass tube *a* twenty-five mm. *outside* diameter and twenty-five cm. long, provided with two glass tubes about six mm. in diameter, one reaching to near the bottom of *a*, sealed in for water inlet and outlet. The tube *a* is surrounded by a stronger glass tube *b* of thirty mm. *inside* diameter sealed on at the top and narrowed at the lower end to a ten mm. tube which extends eight mm. below and is ground off obliquely at the end. About



<sup>1</sup> From advance sheets of the author's thesis, "The Chemistry of the Corn Kernel," for the degree of Doctor of Philosophy, Cornell University, 1898, which will be published as Bulletin No. 53 of the University of Illinois Agricultural Experiment Station.

three cm. from the top of tube *b* a side tube *c* is provided ; it is five cm. long and twelve mm. inner diameter, and is widened, as indicated in the figure, where it is sealed into *b*. The water tubes are cut off at a length of five cm., being blown as indicated to hold a rubber tube.

The outer tube of this condenser is not cooled to a temperature at which atmospheric moisture will condense upon it. This is its chief advantage over the ordinary form in fat extraction with anhydrous ether. The side tube serves to connect with a drying tube.

A few other important points may be noted. The condenser may be used in ordinary distillation by passing the vapor in through the side tube. The ordinary condenser frequently breaks in consequence of the extreme differences in the temperature of the inner tube just above and below the surface of the surrounding water. The new form is free from this objection. The water tubes are both at the top and very convenient for joining up a series of condensers. These condensers are more compact and yet much more effective than the ordinary form, the vapor being distributed in a *thin* layer over a very large condensing surface, the outer tube also acting as an "air condenser."

These condensers have been in almost constant use during the past year in the chemical laboratories of the University of Illinois and have given excellent satisfaction.

There are several condensers which have the water tube inside, but I have found none suited to the purpose for which this was especially designed except that recently described by Sudborough and Feilmann<sup>1</sup>, which is certainly to be preferred to the ordinary form as a return condenser, though it cannot be used safely in distillation.

<sup>1</sup> *J. Soc. Chem. Ind.*, 1897, 16, 979.

## REVIEW.

### SOME RECORDS OF THE YEAR'S PROGRESS IN APPLIED CHEMISTRY.<sup>1</sup>

To present in a single paper even a limited review of what the year has brought forth in the application of chemistry in the arts and manufactures is a difficult task. So manifold have been the discoveries of new facts and the new applications of old ones that to cover all that has been accomplished in the several fields would be beyond the capacity of any individual or of the space or time that could be devoted to a single paper. In the present instance, therefore, it will be possible to present only such as have specially interested the writer and seem to be of interest and value to those to whom this paper may come.

It was said of old "it is not well for man to be alone," and this applies to chemists as well as to those interested in other departments of human activity. Personal exchange of thought and experience is the best stimulus to further endeavor, and so the various meetings and Congresses do their share in the promotion of the interests which most nearly concern us. Of these, several have been held in various localities with most gratifying results. The Third Congress of Applied Chemistry was held in Vienna in the closing weeks of July and was well attended, while the work done was of the highest character. 765 members were in attendance. The Congress was divided into fifteen sections and subsections which held seventy-six separate meetings and discussed, in all, 171 subjects. At the closing session it was proposed and determined that the next meeting should be held in Paris, in 1900. The proceedings of the Congress will be published promptly and will constitute a valuable record of the more important advances made during the year.

Likewise the annual general meetings of the Society of Chemical Industry of England and of the Vereins Deutscher Chemiker of Germany, have been held and the work of these organizations, respectively, will be published in their own Journals.

Chemical industries are perhaps more flourishing and more widely extended in Germany than in other countries though they are becoming far more numerous from year to year everywhere. Doubtless the figures of Wenzel regarding Germany may be accepted as, in a measure at least, reflecting the conditions prevailing throughout all the countries in which such industries flourish. Thus he states that at the close of 1896, in Germany, 96 chemical works with 256,038,900 marks capital gave a total return of 31,495,900 marks in dividends, or an average of 12.3 per cent. against 8.9 for 1897. In these figures the tar

<sup>1</sup> Read before the New York Section of the American Chemical Society, Oct. 7, 1898.

industries gave the highest, nearly 24 per cent., and the fertilizer industries the lowest net returns. The general commercial and financial depression of the past years seem, therefore, to have influenced the chemical industries as well as many others.

In the metallurgical processes but little progress seems to have been made. In the extraction of gold and silver by chemical means the chlorination, bromine, and cyanide processes still hold favored places and they seem to have reached positions having little room for improvement. Most interesting, therefore, is the announcement that Dupre has been able to extract gold with an inexpensive solution containing sodium thiosulphate and ferric halides (chloride, bromide, or iodide) together with an acetate. The mixture of these substances together in water yields a dark red solution capable of dissolving gold and its compounds from sulphide and other ores without attacking the base sulphides. It is stated that a solution containing two per cent. sodium thiosulphate, 0.75 per cent. ferric chloride, and one to two per cent. calcium acetate and diluted to two, three, or even ten times its volume with water, will serve for the extraction of the most varied kinds of gold ore, and that for equal volume and equally exposed gold surface this solution will dissolve, in six to twelve hours, fifteen to twenty times as much gold as a one to two per cent. cyanide solution in equal time. The gold probably passes into solution as sodium gold thiosulphate which may be decomposed for recovery of the gold by zinc, by electrolysis or by the action of sodium nitrate and sulphuric acid. The process seems to be worthy of careful consideration.

The extraction of zinc, particularly when associated with other metals, has always been troublesome and costly and generally impracticable. In this direction more progress has probably been made than in any line of metallurgical work, and several successful methods for the economical and commercial separation of zinc from other metals have been devised during the past year or two. Ashcroft carefully roasts the ore and extracts the roast with sulphuric acid alone or in admixture with ferrous sulphate. The iron salt is decomposed by the zinc oxide, the zinc sulphate passing into solution; the solution obtained by filtration and washing the residue is concentrated until it contains 250 grams of zinc per liter and electrolyzed to removal of 75 per cent. of the dissolved metal. The solution is used on a new lot of ore, or the metal is recovered from it by precipitation. The lead residue is smelted for argentiferous lead.

Siemens likewise roasts the ore carefully, converts the gases into vitriol, extracts the roasted ore with the vitriol produced, electrolyzes the solution to separate the zinc and smelts the residues for argentiferous lead.

Hall leaches the carefully roasted ore with vitriol but he

decomposes the solution with magnesium carbonate, obtaining zinc carbonate which, by heating, he converts into zinc oxide.

Fry, David, and Ledoux, melt the carefully roasted ore with one-fourth its weight of sodium sulphate or bisulphate, and one-eighth its weight of iron oxide in a cupola furnace. It is stated that in the smelting process ninety per cent. of the lead is obtained as metal carrying all the gold and silver, the zinc passing into the fusible slag. The latter is heated with carbon in a Siemen's furnace, the reduced and volatilized zinc burned to oxide, which is collected in dust chambers, resulting in a recovery of eighty per cent. of the zinc. The process is applied in Swansea each week to 400 tons of ore containing twenty to thirty-five per cent. lead, twenty-five to thirty per cent. zinc, thirty ounces silver, and a little gold.

Frank in Berlin extracts zinc electrolytically in a mixed process. He uses a three-cell bath. The anode space contains alkali chloride; the cathode space an alkaline zinc solution and through the intermediate space separated from the others by diaphragms, alkali chloride solution is made to circulate. Zinc is collected at the cathode, chlorine at the anode, and the intermediate space is said to contain chloride and free alkali, the latter to be separated, and recovered by evaporation.

The electrolytic process of Hoepfner is applied to refining of zinc in England, with success and profit. It is stated that one E. P. yields one pound pure zinc, while refining of an equal weight of copper requires only half as much energy.

Tommasi proposes to replace other processes for desilverization of lead by electrolysis obtaining, at the same time, lead of the highest degree of purity. The electrolyte consists of a solution of acetates of sodium and lead. He uses a current of 6.75 volts and 1800 ampères for each bath, and reduces internal resistance by bringing the electrodes closely together. The metal dissolves from the anode, and is deposited on the cathode, whence it is carefully scraped off as cement lead which is fused with carbon, while the silver is deposited as slime. The inventor claims that lead containing 150 to 200 grams of silver per ton, can be profitably worked at a cost of ten francs per ton.

In the extraction of nickel, Mond seems to have made some further progress in the application of the carbonyl reaction. It will be remembered that he first reduces the oxide, and for the more effective action in the subsequent step, this should be done at a temperature not above 350° C.; that he next subjects the reduced metal to the action of carbon monoxide at a temperature of 50° to 60° C. which is most suitable for the reaction producing the carbonyl compound; he then subjects the latter compound to a higher temperature for its decomposition.

He has elaborated an apparatus for practically continuous

operation consisting of a "reducer" and a "volatilizer," but both these may be combined in the same apparatus. In a vertical cylinder are arranged alternately a series of plates and hollow boxes, one above the other. The boxes have the same diameter as the cylinder, and the plates are slightly smaller leaving an annular space at their peripheries. Each box has an opening at the center. A vertical shaft through the center with properly constructed stirring arms forces the material to be treated from the center of the plate to the periphery over which it falls to the surface of the box, and is drawn to its center when it falls to the next lower plate and so on in succession. The boxes are arranged to receive and discharge, at the will of the operator, steam, hot air, or cold water. The boxes of the upper part of the apparatus heat the ore to the reducing point, the boxes at the lower part cool it to the volatilizing point. When properly cooled it is sent to the volatilizer, and the treatment completed. The method seems likely to have practical application.

Storer extracts the metal from New Caledonian ores by heating the finely pulverized ore with ferric chloride solution in a closed vessel to a temperature of  $190^{\circ}$  C., five to eight hours. A solution of nickel chloride containing a little ferric chloride is obtained, and the latter is subsequently removed by lime.

Coehn bases a method for separation of cobalt and nickel upon the fact that in the electrolysis of the solutions containing them the former will separate as peroxide at the anode while the latter will not. Even in the presence of large quantities of nickel the cobalt deposit is free from it. To prevent the deposition of nickel at the cathode, a more easily separable metal such as copper (in form of sulphate) is added to the solution. It is believed that the reaction will find application both in the laboratory and in the works.

Lebeau produces beryllium (glucinum) by electrolysis of its double fluoride of sodium or potassium, using a cathode of nickel and an anode of carbon, and operates at a temperature corresponding with red heat with a current of eighty volts and twenty ampères. The metal obtained contained 99.5 to 99.8 per cent. beryllium, and had a specific gravity of 1.73. It does not oxidize in dry air but burns brilliantly in oxygen. Halogens attack it, and dilute acids dissolve it. It combines at high temperatures with nitrogen, boron, silicon, and carbon, and forms carbides, which with water yield the hydrate and methane. It forms alloys with other metals, those with copper being malleable, and capable of taking high polish which does not readily tarnish in the air.

Goldschmidt and Vautin made use of the very high heat of

combustion of aluminum, which is 360,000 calories, for the production of high temperatures, and the reduction of the very refractory metallic oxides, and by means of it has been able to separate chromium, titanium, manganese, iron, copper, etc. To effect this it is only necessary to intimately mix the finely pulverized oxide with very finely divided aluminum and start the combustion. It proceeds quickly to a finish, producing temperatures up to 3,000° C. and reducing the metals free from carbon.

Franck has likewise utilized the high combustion temperature of aluminum for the reduction of oxides both metallic and non-metallic and particularly for the production of phosphorus. For this latter purpose he mixes the metaphosphate with silica and aluminum, and heats the mixture to start the combustion when the reduction proceeds quietly; the phosphorus distils readily and yields an excellent product particularly when the lime compound is employed.

Various other methods for production of phosphorus have been devised in which the electric furnace is employed to attain the high temperature requisite to proper reduction. Thus Hilbert and Franck and Gin and Leleux, working independently, heat properly proportioned mixtures of phosphatic material and carbon in the electric furnace, the ensuing reaction producing calcium carbide and phosphorus. The phosphorus volatilizes and is collected. Collardeau makes calcium phosphide in the electric furnace, generates hydrogen phosphide with it, and decomposes the gas by passing it through a strongly heated coke-lined tube, and collects the phosphorus liberated; and Boubleque decomposes electrolytically the iron phosphide obtained by fusing together iron compounds and calcium phosphate, and removes the liberated phosphorus by a current of indifferent gas. In Germany the price of phosphorus has further declined and reductions of 0.40 M. for white and 0.80 M. for red are quoted. The production has increased in France, as well as in Russia, is extending to Germany where several works have been projected and the English monopoly is seriously threatened. Likewise at Niagara Falls, and elsewhere in this country, electrolytic processes have been applied and further fall of price may be expected.

Ronco has discussed the various electrolytic methods for production of white lead. From him we learn that Turner Bottome electrolyzes an alkaline salt solution containing sodium or potassium carbonate, between lead electrodes, passing a current of carbon dioxide through the solution during electrolysis. White lead is said to precipitate leaving the electrolyte unchanged. Ferranti and Noad use ammonium acetate as the electrolyte with lead electrodes separated by a diaphragm. After proper time

the anode and cathode liquors are mixed together and carbon dioxide passed through the mixture, and Luckow uses a solution containing one and five-tenths to two per cent. of a mixture of salts consisting of eighty parts of a salt whose acid makes a soluble salt with lead and twenty parts of alkali carbonate. He applies to this solution a current of five-tenths ampère per sq. dm. and two volts between anodes of soft lead and cathodes of hard lead while passing carbon dioxide through the electrolyte.

Progress in the alkali industry has been confined to the electrolytic processes so far as can be learned from the literature. We are told that in England the production of alkali by the Leblanc process has considerably declined while that by the Castner electrolytic process has increased, and the Hargreaves and Bird process gives promise of extension during the present year. The Kellner-Partington Paper Pulp Company at Sharpsborg, in Norway, have projected a large electric plant to utilize the water power of the place. In addition to this a new company, the "Hafslund Aktieskab", has been organized and will erect, on the other side of the falls, an electric plant of 25,000 horse-power, the latter to supply power for works, and for electrochemical works, particularly the manufacture of aluminum and carbide. The status of the utilization of power for generating electric energy for use in the alkali and bleach industries in Europe is illustrated in the following table :

Golling—water-power.....	3000	H. P.	in construction.
Solvay, Bernberg .....	1000	"	in operation.
Solvay, Belgium .....	2000	"	in construction.
Solvay, Russia.....	4000	"	projected.
Castner-Kellner, Runcorn, England .....	1000	"	in operation.
Castner-Kellner, Runcorn, England .....	4000	"	projected and in construction.
Chemische Fabrik, Gresheim, Bitterfeld ....	4000	"	in operation.
Algemeine Electricitäts, Gesellschaft, Bitterfeld .....	3000	"	in construction.
Electro-Chemical Co., St. Helens, England..	1100	"	in operation.

Kellner of Halle, discussing the status of the electrolytic alkali industry in the International Congress of Applied Chemistry in Vienna, states that three processes are now used: (1) Electrolysis of alkali chloride with the aid of diaphragms; (2) electrolysis of a fused electrolyte; and (3) electrolysis of alkali chlorides with the aid of the mercury cathode.

The diaphragms which have given the best results, he says, consist of, first, salt, and second, soap or cement, all having the disadvantage that they need a low tension current, and large apparatus compared with the yield, low concentration of the alkali solution, and finally contamination of the latter with undecomposed electrolytes. He considers that electrolysis of the fused electrolyte leaves much to be desired.



The mercury diaphragm is most used, and has been variously applied by Sindig-Larsen, Castner, Strömers, Rhodin, and others. He denies any objection to their use from a sanitary standpoint, but states that flouring of the quicksilver must be avoided because of the tendency to formation of mercuric chloride with corresponding loss of mercury.

The Hargreaves and Bird process seems to be responding to the persistent work done with it, and shows promise of successful extension and development. Carbon anodes, and iron gauze cathodes are used and between them is arranged a diaphragm of secret constitution and construction. Steam washes the soda from the cathode, and chlorine from the anode is carried to a lime-box. Dr. R. Lucion, of Brussels, reported to the International Congress of Applied Chemistry, that his observations led him to consider that the probabilities of the ultimate successful operation of the process are slight. The diaphragm, he says, apparently consists of an iron screen upon which pulped asbestos has been floated, exhausted by suction and then saturated with a siliceous solution, and the general construction of the apparatus admits of the use of very impure solutions. The capacity of the apparatus referred to by Lucion is elsewhere stated to be: for each cell with ten square meters of diaphragm and cathode surface, decomposition of 106 kilos of salt producing, in twenty-four hours, 117 kilos of bleach of thirty-seven per cent. available chlorine, and 280 kilos crystal or 95 kilos calcined soda. This cell uses a current of 3.9 volts and 2300 ampères equivalent to 14½ E. P., costing \$1.75 daily. The soda contained 97.7 per cent. sodium carbonate and one per cent. sodium chloride. Plans for enlarged construction have been projected but operations have thus far been carried on, apparently, only on a small scale.

Blount discusses the relative possibilities, cost, etc., of the Leblanc soda process and the electrolytic processes, and he finds that while the Leblanc process requires five and three-tenths tons of coal for one ton of caustic and by-products, the electrolytic process consumes but from three and two-tenths to four and two-tenths tons. He considers that although comparison of the two processes is very difficult it may be stated that the electrolytic processes are direct, clean, requiring inexpensive hand labor, and yielding no troublesome by-products, but on the other hand the apparatus required is extensive and costly and rapidly deteriorates.

The chemical processes give large yield with few pieces of apparatus but very large and inexpensive ones, requiring but little repair. Much hand labor is required, and an enormous quantity of worthless and troublesome waste-products result.

In the production of chlorates the electrolytic processes seem to

have taken the lead. Spilker and Lowe using a specially constructed apparatus electrolyze solutions of potassium chloride which in the anode cell is saturated with lime. The saturation of the anode liquid with lime, is maintained in the circulation which constitutes part of the process and the temperature is kept at 40° C when only chlorate is formed. Oettel likewise found that better yields may be obtained with a given current in producing calcium chlorate than is possible with potassium chlorate. Bischoff and Forster find the cause of this to be the lower solubility of the calcium hydroxide produced at the cathode and covering the latter with a thin layer thus minimizing its reducing influence. For best results they recommend a ten per cent. solution of calcium chloride, a current of ten amperes per square meter at the anode, and twice this strength at the cathode because of the calcium hydroxide formed on the latter. If the solution be heated to 50° C. the current tension is found to be the same as for potassium chloride.

Vaubel suggests addition of alkali bicarbonate to the anode liquid when alkali chlorides are being electrolyzed for he finds that in presence of the acid carbonates conversion of chloride to chlorate in the anode cell is complete. While the laboratory experiments gave satisfactory results, they were not confirmed by work on a larger scale.

The number of bleaching agents available in these latter years has been largely increased but much work remains to be done to perfect many of them. The old "bleach" (chloride of lime) still holds its place, yet the new bleaching processes are pushing it very hard. Thus the experiments of Cross and Bevan and of Clayton and Beadle show that bleaching with the Hermite solution consumes less chlorine for a given weight of fiber bleached while the time required for effective operation is enormously reduced. The relative efficiency of the Hermite solution and the chloride solution is as five to three. It was further found that the bleaching solution is more effective when kept in motion and that movement effects a saving of from thirty-seven to forty per cent.

The possibilities of the use of oxygen in its condensed forms seem to be growing with the development of improvements in the generation of electricity. Manufacture of sodium peroxide commercially is extending and the persulphates and percarbonates are attracting deserved attention. The process of Castner or some modification of it seems to be that almost exclusively used in the manufacture of sodium peroxide. The material is used in slightly alkaline solution, excess of alkali being controlled either by magnesium sulphate which is effective or by oil of vitriol.

Little has been added to the work of Marshall and Hansen in

the production of the persulphates and percarbonates. Low temperatures seem to be absolutely essential to their formation and that of persulphuric acid is likewise favored by the addition of small quantities of hydrochloric acid. Practical utilization of these products has not yet been reported. The use of ozone in bleaching is being applied by Siemens and Halske to the treatment of linen and yarns and of starch and its products, and they are devoting special attention to its production.

The production of chlorine by electrolysis is rapidly extending and must eventually, it would seem, replace other processes. The apparatus and methods of Castner and Kellner have found most favor but other and numerous ones have been devised. Yet as already stated practically all leave much to be desired. Hunt and Watson use ferric chloride in the cathode cell with an iron cathode, and potassium chloride in the anode cell and use the chlorine liberated for production of hypochlorite. Haber, on the other hand, electrolyzes strong hydrochloric acid directly and obtains a yield of 100 per cent. If the acid be dilute, hypochlorous acid is formed and with very weak acid oxygen is liberated.

Hammerschmidt and Hess have lately discussed in the *Chemiker Zeitung* the electrolytic production of oxygen, setting forth its advantages and a review of their statements will be of interest. They state that the gas produced by the Brin process contains only ninety per cent. and that obtained by the Linde liquefaction process only seventy-five per cent. of oxygen, and that either method consumes from one to three horse-power hours for the production of one cubic meter of gas.

A perfect electrolytic method remains to be devised, but of those which have thus far been brought forth by d'Arsenoval, Latchinoff, Renard, Dehnard, Siemens Brothers, Garuti and Schuckart & Co., the authors particularly commend that of the last named. The cells employed are of iron and hard rubber, the current used in practice 300 ampères and three and two-tenths to three and three-tenths volts, the temperature of the electrolyte which is a caustic soda solution, 60°C. With these conditions they have determined that sixty kilowatts or ninety horse-power will produce in twenty-four hours 100 cubic meters of oxygen and 200 cubic meters of hydrogen. This involves a plant costing something over \$20,000 and a daily operating expense of between \$30.00 and \$35.00. Garuti's process yields *knall* gas at 4.15 pf. per cubic meter and oxygen at 12.5 pf. per cubic meter. If steam-power is used, twenty-one and sixty-two pf. respectively. Latchinoff likewise electrolyzes a sodium hydroxide solution of ten to fifteen per cent. in an iron vessel using a sheet iron anode enclosed in parchment paper stretched over an ebonite frame. The current tension is two and five-tenths volts and the cost of producing two cubic meters of hydrogen and one

cubic meter of oxygen is estimated at about sixty-five cents. The gases are of a high degree of purity and the processes therefore promise well for the future.

Kassner passes air over warmed calcium plumbate until oxidation is complete, removes residual nitrogen by steam, follows this with a current of carbon dioxide liberating the absorbed oxygen, purifies the latter by well-known means and claims to secure a product testing ninety-nine per cent. Lapointe heats a mixture of caustic soda and manganese dioxide in a current of air, exhausts the gas remaining at the close of the oxidation period, decomposes the manganate with superheated steam, and claims to obtain oxygen free from nitrogen.

Shenstone and Evans discussed, before the London Chemical Society, the influence of electrical tension upon atmospheric air. Under such influence air rapidly contracts, then quickly expands again, containing a trace of nitrogen tetroxide. In the presence of moisture eighty to eighty-five per cent. of atmospheric oxygen may be converted into ozone and with care the conversion may be carried to ninety-eight per cent. If not carried too far no nitrogen tetroxide is formed but there arrives a point at which this occurs. This compound favors the destruction of the ozone by the electric tension. The presence of moisture favors the production of ozone and hinders that of nitrogen tetroxide.

To reduce the temperature of the air and so favor the generation of ozone Andreoli constructs an apparatus with cooled electrodes, the latter consisting of rectangular boxes, each provided with inlet and outlet for cooling liquid and provided with its own circulatory system. Its surface is covered with pointed projections like saw-teeth. The air passes in at the bottom, and out at the top of the chamber in which these electrodes are enclosed.

The same principle influenced Otto in the construction of his apparatus for polymerization of gases and particularly oxygen by the electric spark or a current of high tension. To this end he frequently intermits the current and so prevents heating the apparatus. In one form he arranges two sets of electrodes one of which is fixed, the other parallel with the first and set in sectors of a movable disk. The two sets being properly enclosed and each connected respectively with the poles of a conductor carrying a current of about 18,000 volts, the disk is rapidly rotated causing its set of electrodes to successively pass those of the fixed part. With the current of the tension stated the electrodes should be about three centimeters apart. When the apparatus is in motion and the current is passing, rapid sparking ensues. If air or oxygen be passed between the active surfaces ozone is rapidly produced. In another form of apparatus two concentric cylinders are arranged, one with the electrodes in rings, the other or

inner one with the electrodes set spirally about it. The inner cylinder is made to revolve, and its electrodes rapidly pass in succession those of the outer cylinder. When the current is operating and air or oxygen is passed through the annular space, ozone is rapidly produced. Claim is made: (1) for the use of electrodes arranged, and used as described for effecting polymerization, combination or decomposition of gases, and (2) for producing ozone and other substances; for instance, cyanogen from nitrogen and acetylene, nitrated products from nitrogen and oxygen, ammonia from nitrogen and hydrogen. A similar form of apparatus is said to have been devised for utilization of Lord Rayleigh's plan for obtaining oxidized products from the atmosphere.

We may not leave the discussion of the forms of oxygen without some mention of liquid air which certainly gives some promise of application in an industrial way. It is interesting to note that the process for liquefaction of air depending upon the rapid cooling of the compressed gas by the expansion of a portion from a higher to a much lower pressure should have been brought out almost simultaneously by three different persons in as many countries. Linde in Germany, Hampson in England, and Tripler in this country seem to have attained the same end by the same means at about the same time. The process of Linde which does not differ essentially from that of the others named consists of an air-compressor and a return current apparatus. The air is first compressed to sixteen atmospheres, then to 200 atmospheres, and the water removed from it. Then it is passed through a coil enclosed within a second, the tubes of each coil being concentric. From the inner coil the air compressed to 200 atmospheres is allowed to expand into the annular space between it and the outer coil to sixteen atmospheres, and return to the compressor where it is again compressed to 200. A second compression and expansion reduces the temperature to the critical point and the air is liquefied. The entire apparatus is naturally protected by a non-conducting covering.

The liquid air so obtained contains thirty-seven per cent. oxygen and sixty-three per cent. nitrogen because of the more ready volatilization of nitrogen.

With a Linde machine it is possible to produce a mixture containing equal volumes of oxygen and nitrogen with a consumption of one horse-power for each cubic meter. It has been stated that the European practice yields about three-tenths liter per horse-power which is somewhat better than, so far as we can learn, has been attained in this country. There is no doubt, however, that with better apparatus, and the most economical power generation, much better results are possible.

With the low temperatures available through the rapid evaporation of the liquid air, new fields of interesting investigation of the physical properties of bodies and of chemical reactions, are made possible. Whether the oxygen-enriched mixture can be produced at sufficiently low cost and will be effective enough to be applied to such industrial reactions as the oxidation of hydrochloric acid in the production of chlorine or the oxidation of sulphur dioxide in the production of sulphuric acid as has been suggested, remains to be established; but with proper arrangements for compression and for preservation of the liquid there seems to be no reason why it should not replace other agents, such as ammonia, sulphur dioxide, carbon dioxide, etc., in refrigeration.

In the production and utilization of calcium carbide, some progress seems to have been made; at any rate our knowledge regarding them has been considerably widened. Dr. Sieber discusses the heat requirements and finds a wide difference between those of theory and practice and justifies the efforts being made to improve manufacturing conditions with this regard. He estimates that one E. H. P. should yield 9.38 kilos of carbide in 24 hours, but in practice only four to five kilos are obtained showing that a large portion of the energy employed is consumed in heating the reacting mass. Again practice requires one and three-tenths kilos of carbon and one and four-tenths kilos of lime while theory requires six-tenths and nine-tenths kilos respectively, for one kilo of carbide. The power consumed, therefore, becomes 3230 watt-hours for heating and 1900 watt-hours for reaction. One E. H. P. should, therefore, yield in twenty-four hours 3.44 kilos. Since in the generation of electrical energy scarcely more than fifteen per cent. of the fuel energy is realized, it is plain that economy requires that the materials used should be heated before they enter the furnace and are subject to the action of the current. He suggests the use of the carbon monoxide generated for this purpose. If water-power is available, of course this is of less importance. Pictet likewise realized the importance of this, and has devised a specially constructed furnace having it in view. Into his furnace he charges coke and lime, the former being in considerable excess over that required for the final reaction. Into the upper of three zones he injects air, and by the resulting combustion of the excess of carbon a temperature of  $2,000^{\circ}\text{C}$ . is attained. Into the next lower zone he injects oxy-hydrogen gas, the combustion of which produces a temperature of  $2,300^{\circ}$  to  $2,400^{\circ}\text{C}$ . In the bottom zone are arranged electrodes with the arc immediately over an outlet. The carbide formed flows out through the opening and is collected underneath. Practical results of use of the furnace have not been given.

Hausermann recommends casting the carbon and lime into blocks or sticks before charging to the furnace, the principal object being to avoid production of partially converted dust which thus far has found no valuable application.

Regarding the cost of calcium carbide Desiré Korda states that one horse-power day should produce four kilos of carbide which would bring the cost to about \$50 per ton.

The Neuhausen Company quotes the product at 300 francs, say \$60 a ton. The author considers that the cost claimed by certain American producers is too low but the exports of the product from this country would not seem to confirm this.

It is now generally accepted by the best authorities that much of the danger and loss incident to the manufacture and use of acetylene is to be ascribed to the high temperatures produced in the generators employed. Gerdes reports that determinations of heat generated in the decomposition of calcium carbide shows it to amount to 1,200 calories for each kilogram of gas liberated. Lewes, operating with an apparatus of his own device, concludes that 406 calories fairly represent the heat of decomposition of one kilo of commercial carbide and he estimates that for pure carbide the figure should be 444.6. This varies somewhat from that given by Gerdes but the observers doubtless had different qualities of carbide. At any rate it is evident from the figures given that the temperature in the generators may readily reach the danger point. Pure acetylene suffers decomposition at  $780^{\circ}$  and Gerdes states that when mixed with a certain quantity of air this may even occur at  $480^{\circ}$ . Lewes, in a large series of experiments, found the temperatures in generators, in which a comparatively small quantity of water took part in the reaction, rose to from  $703^{\circ}$  to  $807^{\circ}$  in different cases. Under such circumstances, deBrevans states that polymerization occurs with the production of liquid hydrocarbons such as benzene, styrolene, etc., reducing the illuminating power. Acetylene produced by Lewes in his experiments and analyzed by him contained :

	I.	II.
Acetylene .....	70	69.7
Saturated hydrocarbons .....	11.3	11.4
Hydrogen .....	18.7	18.9

He states that this change reduced the illuminating power from 240 candles to about 126. Benzene is the principal product of the decomposition and is the most conducive to difficulties, such as stoppage of pipes by its condensation, of the burners by its decomposition, giving tarry products and giving smoky flames. Both Gerdes and Lewes recommend the use of large volumes of water in the generator, allowing the carbide to fall into the water ; both recommend that the temperature shall not rise above  $100^{\circ}$  in the generator. Pictet even recommends that

the water used shall be cooled at  $10^{\circ}\text{C}$ . and be maintained at this temperature within the generator by special arrangement to that end. Bamberger likewise recommends using large quantities of water into which the carbide may fall in order to reduce the generation of ammonia from the nitrides and cyanides.

The poisonous qualities of commercial acetylene are believed to be due to the phosphorus and sulphur compounds it contains when recently generated. So likewise the dangerous character of the gas and its explosiveness are believed to be due to the presence of these compounds. This latter view is not sustained by the results of the experiments of Lewes which showed that in order that the gas may become spontaneously inflammable from such admixture it must contain over eighty per cent. of hydrogen phosphide. Lewes observed however that cases of spontaneous ignition occurred in the generation of gas when the carbide used contained even as low as one per cent. of calcium phosphide. Yet in spite of this fact, he expressed the opinion that ordinary commercial carbide could be used without danger from this cause.

Hubou finds the impurities of calcium carbide to be lime and coke, carborundum, silicides, nitrides, phosphides, arsenides, and sulphides. Lewes found the same impurities. It is natural therefore that the gaseous products of decomposition of these substances by water should be found in acetylene. So Girard found that gases containing 95.9 to 99.5 per cent. of acetylene, four-tenths to two and nine-tenths per cent. of nitrogen, 0.08 to 1.19 per cent. of carbon monoxide, and no oxygen, contained likewise per cubic meter two and seven-tenths grams of ammonia, 0.44 to 1.78 grams of hydrogen phosphide, 0 to 13.42 grams of hydrogen sulphide. Lewes found an average of 0.65 per cent. of hydrogen phosphide between limits of 0.02 and 2.30 per cent. DeBrevans found hydrogen phosphide, silicide, and sulphide, ammonia, ammonium sulphide, sulphur dioxide, cyanogen and sulphocyanogen compounds, and these results have been confirmed by Vertess, Bamberger, and others. Bamberger ascribes the presence of ammonia and cyanogen compounds to the nitrides and even cyanides formed in the furnace. Nitrides of aluminum and magnesium decompose in presence of water, forming ammonia. The cyanides, which he says are quickly formed when hot carbide is exposed to nitrogen, are readily decomposed by superheated steam to form ammonia. He therefore recommends maintenance of low temperature in the generator, letting the carbide fall into a large volume of cold water which will leave the aluminum nitride and the cyanides undecomposed, and by which the small quantity of ammonia liberated may be absorbed.

For the purification of acetylene many suggestions have been



made and several processes proposed. Oderheimer uses something like the Laming mixture of sawdust and iron compounds which seems to reduce the tendency of the gas to give smoky flames but it does not remove the phosphorus compounds. Lunge and Cedercreutz easily remove the hydrogen phosphide by passing the gas over wet calcium chloride and afterwards through lime to hold back the chlorine. Frank finds that the phosphorus and sulphur compounds may be reduced to a minimum by washing with acid metallic salt solutions and Pictet uses, in succession, the following liquids: (1) a very concentrated solution of calcium chloride, (2) solution of lead compounds, and (3) sulphuric acid. All the solutions are cooled to  $-16^{\circ}$  C. at which temperature he finds the impurities are absorbed while the acetylene is not.

It is held that the thoroughly purified acetylene will form combinations with neither copper nor other metals, and is even less poisonous than ordinary illuminating gas; but in presence of air or moisture combinations with metals are likely to be formed, and these substances should therefore be carefully excluded.

Both Pintsch Co. and Pictet have specially studied the sensitiveness of the gas when compressed to heat and shock. The Pintsch Co. filled a vessel whose joints were soft soldered, the pressure within being six atmospheres. When heated to  $200^{\circ}$  the solder melted and the gas issuing from the opened joint burned quietly; but another vessel with hard soldered joints, likewise filled with pressure of six atmospheres, laid upon a burning wood-pile, ultimately exploded with the greatest violence. Pictet cools the gas to  $-20^{\circ}$  C. as it comes from the gasometer, separates the moisture, forces it at eight atmospheres through a cooling system, bringing it to  $-80^{\circ}$ , at which temperature and pressure it becomes liquid. It is stated that the containing bombs which, by the way, were fitted with brass cocks, were pierced with rifle bullets, struck with mallets, and hurled against rocks without causing explosion.

But the Pintsch Company recommends, as a further measure of safety, that for use in railway lighting the gas be mixed with oil-gas in the proportion of thirty per cent. of the former to seventy per cent. of the latter. Claude and Hess find that while acetone will dissolve at  $15^{\circ}$  C. about twenty-five times its volume of acetylene, if the pressure be increased to twelve atmospheres it will hold 300 times its volume. That is to say one liter of acetone is capable of holding 300 liters of acetylene or the quantity ordinarily liberated from one kilogram of carbide. The acetylene thus held will be given off with release of pressure until solubility at atmospheric pressure is reached. The mixture is said to be practically non-explosive, and therefore much safer

than liquefied acetylene, but it is suggested that before use it be washed to remove the accompanying acetone.

Concerning the relative efficiency of acetylene as a practical illuminating agent much has been said. Hubou finds that ordinary burners of different lighting powers consume of acetylene per candle-power hour :

Burners of 1 to 2 c.p.	Acetylene consumed.	
	Liters.	
" " 2 to 5 "	8	
" " 5 to 10 "	7.5	
" " 5 to 10 "	7.0	
" " over 10 "	5.6	

Pictet offers a table of comparison of cost of the various sources of light used in Paris based upon prices of illuminating material as follows : Calcium carbide, 0.4 franc per kilogram ; acetylene, 1.5 francs per cubic meter ; petroleum, 0.97 franc per kilogram ; illuminating gas, 0.3 franc per cubic meter ; incandescent electric light, 1.0 franc per kilowatt hour.

The ratios of cost of these different materials as used to acetylene are respectively as follows : Normal lamp, 4.4 : 1.2 ; petroleum round-wick lamp, 7.7 : 3.6 ; Argand gas burner, 3.8 : 1.2 ; Paris burners, 6 : 6 to 9 : 11.2 ; Wenham lamp, 5.1 : 5.5 ; Welsbach light, 2.6 : 3.4 and 3.6 : 5.6 ; incandescent electric, 3 : 1.2.

Wedding's table of comparisons illustrate these same relations as they appear in Germany and will be of interest :

	Candle-power.	Heat per candle-power.	Cost per hour.
		Cal.	
Illuminating gas-slit burner.....	30	66.5	6.4
" round burner .....	20	50.	3.2
" regenerative burner .....	111	18.4	6.5
" incandescent burner....	50	10.	1.6
Spirit incandescent lamp .....	30	10.6	2.0
Kerosene .....	30	32.0	2.2
Kerosene incandescent lamp .....	40	13.75	1.0
Acetylene .....	60	8.9	5.4
Electric light incandescent .....	16	2.59	2.9
" " arc light .....	600	0.37	15.5

These figures are less favorable to acetylene than those of Pictet.

Ten French factories are making calcium carbide for the production of acetylene gas and four are being built. France next year will produce three thousand tons of the carbide, worth \$75 a ton, exclusive of the cost of packing. Two villages in France are lighted wholly by acetylene gas. Each house in these villages has its own gas plant, just as bicyclists in this country make their own gas from the carbide. The lighting power of acetylene is fifteen times that of coal gas. For the same amount of light it costs 50 per cent. less than coal-gas.<sup>1</sup>

<sup>1</sup> This paragraph is quoted from a despatch to one of the current daily journals. M.

Krämer discussing the production of benzene as a by-product of the coking industry says that the yield of 4500 to 5000 tons in a single year caused the price to fall to twenty-five marks per 100 kilograms, the quantity being three times as much as is obtained in Germany from gas-tar. To utilize the excess he recommends its admixture with alcohol, adding ten per cent. (10 : 1) for use in incandescent lamps. Frank states that the Charlottenberg Gasanstalt found that when added to illuminating gas of thirteen to fourteen candle-power, four grams sufficed to increase the lighting capacity, one candle-power. Schimming and Jaeger, found that mixed water-gas and coal-gas required seven to eight grams benzene for one candle-power increase. Krämer however showed that water-gas free from methane will not hold benzene effectively.

The discovery of Nernst that when calcium and magnesium oxides are heated they become tolerably good conductors of electricity and that when further heated by the transmission of a current they become highly incandescent is most interesting. Even at the highest white heat they are not softened or materially changed. If the carbon filament be covered with a layer of magnesium oxide and enclosed in a vacuum globe the oxide becomes heated and finally incandescent. Such a rod gives with a current of 0.25 ampère and 108 volts a light of twenty-eight Hefner candle-power or one candle-power per watt while the ordinary incandescent lamp consumes three to four watts per candle-power. The initial heating of the magnesium oxide presents difficulties, and the life of the filament is questioned.

Auer von Welsbach utilizes in his incandescent light the hitherto unknown property of osmium *in vacuo* and in a reducing gas mixture to resist liquefaction or volatilization even at the volatilization points of iridium or platinum. Since the light emission of a glowing body grows much more rapidly than its absolute temperature it is held that good light effects should be obtained by the use of osmium filaments instead of carbon filaments in the incandescent lamps. The same observer finds that platinum wire will not melt even at the most intense white heat if covered with only so much as one-tenth millimeter of thorium oxide. It would therefore appear that even more easily melting bodies than osmium may be used for the preparation of filaments to stand particularly high temperatures.

Altogether the status of the illumination problem has materially changed within the year, and decided progress may be expected in the very near future.

In the production and recovery of the nitrogen compounds, some progress has been made. It is reported that in England the production of ammonia as sulphate in 1897, from different sources respectively was as follows :

	Long tons.
From gas works.....	132,724
“ iron “ .....	17,729
“ shale “ .....	37,153
“ coke “ .....	10,624

It is also reported that in Europe the production in 1898 will exceed 375,000 tons of sulphate against the production of 330,000 tons in 1897. Of this, Germany and Austria produced 100,000 tons; 46,000 tons from Eschweiler and the Saar, 40,000 tons from upper and lower Silesia and Austria, and 14,000 tons from gas works.

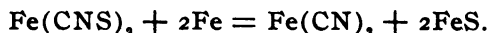
These must remain for some time the principal sources of the ammonia compounds, yet we must expect that the utilization of other waste products may contribute at least a small share. Thus, Pieper and Fellner propose to collect the gases issuing from the dry distillation of nitrogenous organic matters as well as those from nitrogenous coke. One-third of the nitrogen passes off, they say, with the hydrocarbon gases, and the remainder is removed by superheated steam in an apparatus specially designed for the purpose.

In the fixation of atmospheric nitrogen, attention has already been called to the results of Lord Rayleigh which showed that if the nitrous compounds generated in the atmosphere be promptly removed from the sphere of action of the spark by means of an alkaline solution the yield becomes attractive. During the past year Berthelot has continued his researches in this direction. His investigations into the fixation of nitrogen by carbon compounds and particularly the carbohydrates under the influence of electrical tension such as prevails in the Siemens tubes are well known, and are of the highest interest. He has now extended them to the study of the alcohols, ethers, phenols, and similar compounds and finds that under the influence of the electric spark in an atmosphere of nitrogen containing vapors of the substances named, nitrogen is fixed and hydrogen liberated; in other words true substitution is effected, the quantity of nitrogen fixed varying with the different compounds. The action is here doubtless similar to that occurring in the Otto apparatus already mentioned and illustrates further the influence of the electrical tension upon the intensity of chemical action, adding thus to the future applications of the current.

In the production of the cyanides from atmospheric nitrogen, but little by way of suggestion or improvement has been offered. Blackmore proposes to produce cyanides, ferrocyanides, and thiocyanates by fusing together a mixture consisting of metallic sulphides and carbides, and passing nitrogen gas through the mixture. He recommends an alkaline sulphide and iron carbide for the purpose. Petschow melts alkali in a crucible and introduces nitrogen mixed with hydrocarbon gases, such as

acetylene, or with carbon dust, to the melt through an opening in the cover. He avoids excess of carbon, but does not limit the quantity of nitrogen or ammonia used. Excess of the latter is to be collected in acid, and the cyanide recovered by well-known methods. Colné, of Pittsburg, proposed a method for production of cyanide and ammonia in the following steps carried on in a closed alkali furnace: (1) burning of air and gas, (2) dissociation of liquid hydrocarbon, (3) dissociation of alkali and formation of cyanide. In connection with this, decomposition of the cyanide with superheated steam for producing ammonia. Caro passes free nitrogen over barium or calcium carbide alone, or over these substances mixed with alkali and carbon, the whole heated in a clay retort or tube to a dark red heat. Rossel and Franck heat the carbides of aluminum, magnesium, zinc, or iron in presence of nitrogen to form the corresponding nitrides.

Conroy, Hurter, and Brock convert the thiocyanate into cyanide by heating together in an autoclave under pressure, calcium thiocyanate and ferrous chloride, but preferably the thiocyanate and reduced iron in excess, with the following reaction:



The residuum is treated with soda-lye and leached to obtain sodium ferrocyanide; or the mass is treated with weak hydrochloric acid, the hydrogen sulphide collected, the ferrous cyanide washed and treated with alkali. If the ferrous chloride is used in the first process the residue from the soda leach is treated with hydrochloric acid, and the resulting ferrous chloride used as indicated.

The United Alkali Company have utilized the reaction of nitric acid with the thiocyanates for the production of pure cyanide. The solution of 20 to 30 per cent. thiocyanate is mixed with an excess of nitric acid and forced in fine spray into a closed vessel containing hot water and fitted with a stirring gear. Air must be vigorously excluded from the apparatus, the thiocyanate is broken up, sulphuric acid is formed, cyanogen gas is liberated and the latter after being washed to free from nitrous fumes is absorbed in an alkaline solution or cold water.

Nithack, of Nordhausen, undertakes the production of nitrogen compounds by the electrolysis of water charged with air, making use of an observation of Davy to the effect that under such conditions ammonia will be formed at the cathode and nitric acid at the anode. He therefore electrolyzes water charged under pressure with air and claims to so obtain ultimately a strong solution of ammonia salt.

What seems to be an improvement in the manufacture of oxalic acid has been patented in the United States and England. Woody matter is dried and heated, *in vacuo*, to 70° C. to remove

air. Hot alkali liquor is then run in upon it, the vacuum maintained, and temperature raised to  $180^{\circ}\text{C}$ . The progress of the operation is controlled by testing a sample from time to time. When the digestion is complete oxidizing substances such as hydrogen dioxide, sodium dioxide, air, or ozonized air, are introduced while the vacuum is maintained. The resulting product is treated according to the usual process of oxalic manufacture. The industrial value of the process remains to be determined.

The growing prejudice of the French medical fraternity in favor of higher value of white wines for human consumption has stimulated their production and to the extent of removing the color of wine from red grapes. To this end Martinaud extracts the juice thoroughly, aerates it until it is completely decolorized, filters it to remove the precipitated coloring-matter, and ferments the resulting liquid. The special advantage of the white wine thus made is not stated.

Buchner, of Tübingen, has made the interesting discovery that the process of alcoholic fermentation is not purely physiological and part of the vital function of the yeast plant, but is due to the influence of an enzyme produced within and secreted by the living cell. He mixed beer yeast with fine sand, ground the mass till the whole was well reduced, subjected it to pressure of 500 atmospheres, and so obtained 450 grams of juice, which was yellowish, transparent, almost clear—but sometimes somewhat opalescent—having pleasant odor and containing carbon dioxide and not a little coagulable albumen. Among other enzymes there were present invertin and maltose and glycogen hydrolyzing ferments besides oxybases. When sugar is added to the juice fermentation is set up much more quickly than with fresh yeast and the liberated gas is pure carbon dioxide. Its action upon sugar is lost in two or three days, but in presence of sugar it continues five or six days. It may be dried without losing its power. Yeasts differ considerably as regards the juices they yield and the juices of some cells have no fermenting power.

More interesting and valuable to the industry is the discovery of Dr. Calmette of Lille, France, of a micro-organism which has the power of converting starch directly into alcohol without the previous intervention of malt or other hydrolyzing agent. He practically applied his discovery in a distillery where 250 kilograms of grain gave 10,000 liter per cent. of alcohol (100 liters of absolute alcohol). If this operation and result can be duplicated it will eliminate from the distillery the use of malt and greatly diminish the cost of production of alcohol. The yield of alcohol reported is attractive being about as high as is ordinarily obtained in the distilleries of either this country or Germany and the new ferment will doubtless receive serious attention from those directly interested in the development of the spirit industry.

The promise of the production of spirit from moss, peat, waste

woody matter, etc., has not been fulfilled, and the results of Stenberg, of von Felitzen and Tollens, and of Simonsen give but little encouragement to the industry. Tollens, ascribes the unexpectedly low yields of alcohol obtained in each case to the presence of pentoses in the crude materials, which, although converted by the acid treatment, yield products incapable of alcoholic fermentation. Thus Tollens in his study of peats made determinations of the total reducing substances and of the pentoses and found that the difference between the results corresponded closely with the fermentable carbohydrates as indicated by the alcohol obtained. And Tollens' results correspond closely with those obtained by Maercker.

The process of Fritsche for producing alcohol from ethylsulphuric acid obtained from washing the ethylene from coke-oven gases has not further developed notwithstanding the possible low cost of the product and this has been ascribed to the limited supply of the raw material. It is estimated that the total theoretical production from this source could not exceed 5,000,000 gallons of absolute alcohol; but it has been suggested that a further source of ethylene would be possible in the reaction between calcium carbide in an acid solution containing zinc or some other metal, whereby it is expected that the nascent hydrogen and nascent acetylene might combine with formation of the compound sought. The resulting ethylene was to be treated after the method of Fritsche for production of alcohol. The cost of operation of this process would doubtless preclude its use even with very low cost of calcium carbide and therefore of acetylene. It is impossible to say however what the future may have in store for us in this particular, for with cheap acetylene on one hand, with cheap hydrogen from the electrolytic processes of Latchinoff, Garuti, or of Schuchert & Co., together with electrical apparatus of Otto for intensifying chemical activity, cheap and abundant ethylene may still be possible. The suggestion will doubtless be attractive to those most closely interested.

In every direction industrial progress is suggestive, and we may expect advancement in all directions with increasing intensity. Commercial artificial indigo, commercial artificial silk, commercial mercerized cotton in its various forms, the new colors and medicinal substances from the carbon compounds, new concentrated nutritive substances, synthetic albumen, the various toxins and extracts of animal matters of therapeutic value, all claim a large share of attention; and so do hundreds of other substances and processes in which the principles of chemistry find application to human needs but they must, for such discussion as this, be left to other hands and for other occasions in the hope that neither may be wanting to fill the gaps necessarily left by the present effort.

WM. MCMURTRIE.

## NOTE.

*Standard Pig Iron Samples.*—The Committee appointed by the American Foundrymen's Association to prepare and distribute standard samples of pig iron drillings, reports that it is now able to distribute a range of samples that will meet the approval and indorsement of managers and chemists employed in the iron industry.

The standardized samples now ready for distribution cover the following determinations :

Silicon, one each of a low, medium and high range of cast iron.

Sulphur, one each of a low, medium and high range of cast iron.

Manganese, one each of a low, medium and high range of cast iron.

Phosphorus, one each of a low, medium and high range of cast iron.

Total carbon, one determination.

Graphite, one determination.

Titanium, three determinations.

In all, seventeen determinations made on four (4) samples.

The samples are designated as A, B, C, and D. Sample A, which has been ground to pass a 40-mesh sieve, gives one total carbon and one graphite. Sample B gives a low silicon, a medium sulphur, a low manganese, a phosphorus which is within the Bessemer limit, and a titanium. This has been passed through a 20-mesh sieve. Sample C gives a medium silicon, high sulphur, medium manganese, medium phosphorus, and a titanium. This has also passed a 20-mesh sieve. Sample D gives a high silicon, low sulphur, high manganese, high phosphorus, and a titanium, and has passed through a 40-mesh sieve.

The drillings were obtained from castings made after the plan described by Mr. West in his paper before the Pittsburg Foundrymen's Association, June, 1898. The drillings were prepared under the supervision of Prof. C. H. Benjamin, and the standardizing under that of Prof. A. W. Smith, both of the Case School of Applied Science, Cleveland. The chemists engaged in standardizing the four samples were Messrs. Booth, Garrett, and Blair, Philadelphia ; Prof. A. W. Smith, Cremer and Bick-



nell, Cleveland, O., and Andrew S. McCreath, Harrisburg, Pa.

These samples may be obtained of Thos. D. West, chairman, Sharpsville, Pa.

E. H.

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### NOTICE.

The regular monthly meetings of the New York Section will be held in the Chemical Lecture Room of the College of the City of New York, 17 Lexington Avenue, at 8.15 P.M. on the following dates: January 13; February 9; March 9; April 7; May 5; June 9. All chemists who may be visiting New York on the dates named are cordially invited to attend these meetings.

WM. MCMURTRIE.

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### NEW BOOKS.

SOAPS. A practical manual of the manufacture of domestic, toilet, and other soaps. BY GEORGE H. HURST, F.C.S. London: Scott, Greenwood & Co.; New York: D. Van Nostrand Co. Price, \$5.00.

Nearly half this book is devoted to the raw materials used in the manufacture of soap. This part is very comprehensive, containing even a chapter on water as a soap material; at the same time no space is given to technically useless descriptions of those fats and oils, which are but rarely used in soap manufacture, while the position of the commoner fats in the scale of usefulness is clearly stated.

Considering the admirable arrangement of this part of the work, it is to be regretted that it is not more accurate, especially in the chemistry of the fats, for though the author has inserted abundant simple formulas and equations, many passages show that the material has been hastily compiled from the various works on this subject; for instance, with a little thought the author would have avoided the erroneous statement made on page 117 that the proportion of solid fatty acids in tallow is *increased* by the addition of cottonseed-oil stearin. Again, lard is said to contain thirty-five to forty per cent. of stearin with small quantities of palmitin, while actually, as a more careful search into the literature of this subject would have shown, the palmitin in lard is largely in excess of the stearin. Such errors are common in works on this subject, but it is time that they were weeded out.

One chapter is devoted to "Soap Machinery," and another to the "Technology of Soap-Making." This subject, always difficult to treat in a manual, gives the novice a clear view of the principles and practice of soap-making.

In the analysis of soap the author shows himself to be entirely at home, writing from his own experience. Indeed, a single brief chapter of more use to the soap chemist can hardly be found anywhere. The practice of calculating the alkali combined with fatty acid as Na or K instead of the time-worn  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ , is to be commended; for, besides being the modern and rational view of the composition of alkaline salts, it allows the fatty acid to be entered in the analysis as such, instead of as hypothetical anhydride, the total, on footing up the analysis, being only a trifle over 100, due to the acid hydrogen of the fatty acid.

A very brief chapter is given to the recovery of glycerine from lyes, and an appendix is added with the common specific gravity and hydrometer tables. E. TWITCHELL.

### BOOKS RECEIVED.

Some Notes on Chemical Jurisprudence. A digest of patent-law cases involving cases. By Harwood Huntington, 260 West Broadway, New York City. Price, 25 cents.

Outlines of Industrial Chemistry. A text-book for students. By Frank Hall Thorp, Ph.D. New York: The Macmillan Co. 1898. xx+541 pp. Price, \$3.50.

Preliminary Report of an Investigation of Rivers and Deep Ground Waters of Ohio as Sources of Public Water Supplies, by the State Board of Health, 1897-1898. Cleveland, Ohio. 1898. 259 pp. with maps.

A Report of Progress of Investigations in the Chemistry of Wheat. By G. L. Teller. Bulletin No. 53. Arkansas Agricultural Experiment Station, Fayetteville, Ark. September, 1898. 30 pp.

Report on the Investigations into the Purification of the Ohio River Water at Louisville, Kentucky, made to the President and Directors of the Louisville Water Company. By George W. Fuller. New York: D. Van Nostrand Company. 1898. 4to. vii+461 pp. Price, \$10.00.

Digest of Criticisms on the United States Pharmacopoeia: Seventh Decennial Revision (1890). Part II, comprising abstracts of papers up to December 31, 1897. viii+146 pp. Published by the Committee of Revision and Publication of the Pharmacopoeia of the United States (1890-1900).

Chemische Technologie an den Universitäten und technischen Hochschulen Deutschlands. Von Dr. Ferdinand Fischer, Professor an der Universität Göttingen. B-aunschweig: Friedrich Viewig und Sohn. vi+54 pp. Price, M 1.25.

Report of the Secretary of Agriculture. 1898. Washington: Government Printing Office. 1898. 60 pp.

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